FOURTH QUARTER AND FINAL REPORT

DEVELOPMENT OF SECONDARY CADMIUM-OXYGEN CELLS FOR SPACECRAFT APPLICATIONS

(31 MARCH 1967 - 31 MARCH 1968)

CONTRACT NO. NAS-5-10384
for
GODDARD SPACE FLIGHT CENTER
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GREENBELT, MARYLAND

by

UNION CARBIDE CORPORATION
CONSUMER PRODUCTS DIVISION
RESEARCH LABORATORY - PARMA, OHIO

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APPROVED BY:

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ABSTRACT

A feasibility study of the cadmium-oxygen system has been carried out. The system has been found to produce from 0.92 to 0.70 volts at from 1.5 to 40 ma/cm^2 respectively. The majority of tests have been conducted so that the cadmium anode was completely discharged on each cycle. The test cells have consistently given at least 65 per cent coulombic efficiency of the anode. Cycle life has been limited by the cathode or oxygen electrode.

The anode used throughout the test program was electrodeposited cadmium on a conductive screen or mesh material. Copper, silver and nickel base materials have been used, but most of the anodes have been deposited on nickel screen. The anodes were made according to Union Carbide's patented process[(1)]. Normally anodes with a capacity of 0.031 amp-hr/cm^2 have been used, but electrodes with a capacity of up to 0.121 amp-hr/cm^2 have been made and tested. Standard tests use 3" x 3" x 0.030" electrodes with an initial actual capacity of 2.0 amp-hr.

Two types of cathodes have been tested. One of these was purchased from the American Cyanamid Co.and is designated as"LAB-40". Using this electrode, a two-electrode cell structure was developed and tested in single cells. Cycle life,which is limited by cathode polarization and electrolyte leakage, has ranged from 10 to 70 cycles at 0° C, 100 to 300 cycles at 25° C and 90 to 275 cycles at 40° C on a 2-hour charge/2-hour discharge schedule. Raising the cutoff limit of the charging voltage can extend the cycle life considerably at about 50% of the rated capacity. The degradation of the American Cyanamid electrode is believed to be related to wetting of the catalytically active portion of the electrode.

The second type of cathode was a Union Carbide T-2 electrode in which the catalytically active portion is a plastic-bonded carbon layer. Since this carbon layer would be destroyed if oxygen were evolved from it during charging, a three-electrode cell structure was developed in which the anode is charged against an inert third electrode of nickel. Here, also the cycle life is limited by the cathode, wherein the failure is due to severe leakage through the cathode. The normal cycle life of 2-hour charge/2-hour discharge has been from 50 to 90 cycles at 0° C, 400 to 600 cycles at 25° C, and 150 to 250 cycles at 40° C.

Operating voltages have also been determined for 24-hours/24-hours, 22-hours/2-hours, and 2-hours/22-hours charge/discharge regimes. On some of these regimes cycle life is still not complete for cells with American Cyanamid electrodes. These cells were started late due to delays in electrode delivery. The Union Carbide T-2 electrode has given about 2500 hours of service on all regimes at room temperature.

Cells of both two- and three-electrode types have been built and tested in which the only electrolyte contained in the cell was that capable of being held by capillary action. It has been found that asbestos is not a satisfactory wick-type separator for this system because of an interaction with the cadmium anode. Nonflooded cells of this type show promise of improving cathode performance.

A few capillary filled cells have been tested in enclosed containers wherein the oxygen generated on charge was reused on discharge. As of the end of the contract period the best cell of this type had completed only 28 cycles on a 4-hour charge/4-hour discharge cycle and 6 cycles on a 2-hour charge/2-hour discharge cycle and is continuing to function well*. The charge and discharge currents on the 2-hour rate are 700 ma (17.7 ma/cm^2) charge and 600 ma (15.2 ma/cm^2)discharge.

A number of single cells of both the two- and three-electrode types have been built and shipped to NASA to complete the prototype requirements of the contract. Descriptions of these cells and operating instructions are included as Appendix I of this report.

In general, the three-electrode structure shows greater stability with cycle life and normally gives longer cycle life than the two-electrode system. Also, the Union Carbide T-2 electrode is lighter than the American Cyanamid "LAB-40". However, because a third electrode is necessary with the T-2, causing increased weight and a greater volume of electrolyte, and because of more complex wiring, the two-electrode structure has been chosen for design study considerations.

* Continuing to operate efficiently on a 2-hour charge/2-hour discharge regime, the cell described has completed 1300 cycles as of November 29, 1968. Discharge current was reduced to 500 ma (12.7 ma/cm^2) after 735 cycles.

Single cells of nominal 2.0 amp-hr capacity have been built and tested with an energy density of as high as 7.0 watt-hr/lb including case and terminals, but excluding oxygen tankage. A design study for a 3 KWH battery for space applications has been completed (see Appendix II) and shows an energy density of 19.55 watt-hr/lb. of battery including tankage and auxillary equipment.

INTRODUCTION

The technical approach is based upon Union Carbide's background experience in fuel cell technology, in the "Air Cell" and in various rechargeable battery systems. The cadmium- oxygen system was selected as the best system for spacecraft application because of its long cycle life, even on deep discharge. With a theoretical energy density of 235 watt-hrs/lb, the cadmium-oxygen system has a higher energy density than the nickel-cadmium system.

Two types of oxygen electrodes have been employed in the present work; (1) the thin "fixed-zone" plastic-bonded carbon electrodes developed by Union Carbide[2-5] and, (2) fuel cell electrodes developed by the American Cyanamid Company designated as "LAB-40" or "LAB-6". The cadmium electrode was previously developed and successfully employed in nickel-cadmium batteries[1]. All materials used in the cells are readily available from domestic suppliers.

The program has shown the feasibility of recharging the cadmium-oxygen system. Work has been done on parallel programs exploring a two-electrode and a three-electrode experimental cell construction. In the two-electrode cell, the oxygen electrode used is the American Cyanamid LAB-40 or LAB-6. A new supply of American Cyanamid electrodes with an improved backing material was purchased, but because delivery was not made until very late in the Third Quarter some of the two-electrode cell tests are still being cycled. The three-electrode cell is constructed so that the cathode is idle during the charge part of the cycle while a third inert electrode carries the charging current. Union Carbide cathodes are usually used in the three-electrode system.

DISCUSSION

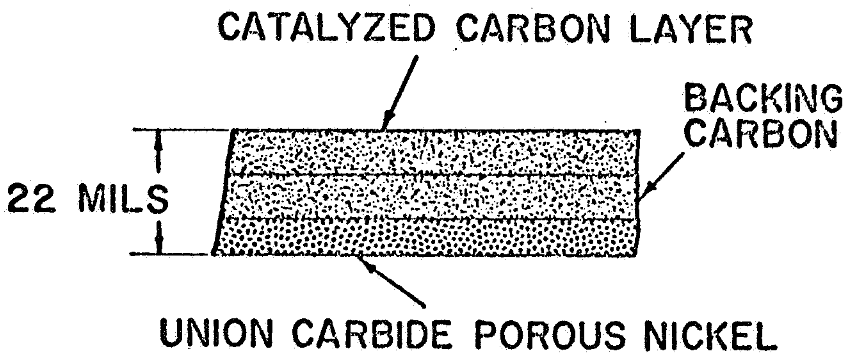
A. Description of Components

1. Oxygen Electrodes

Two types of oxygen electrodes have been used in cells tested to date. One is the Union Carbide "fixed-zone" electrode which consists of an electrochemically active carbon layer applied to a porous metal backing[2-6]. The electrode is illustrated in Figure 1. Because of its susceptibility to damage from oxygen evolution which occurs during charging, it is necessary to use a third electrode as the charging electrode.

FIGURE 1.

CROSS-SECTION OF THIN "FIXED-ZONE" ELECTRODES



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The other oxygen electrode was purchased from the American Cyanamid Company. This electrode is composed of a catalyzed electrochemically active material bonded with TEFLON, molded onto a gold-plated nickel screen collector and backed with a porous hydrophobic material. Electrodes with two designations have been used; (1) "LAB-40" which has been predominantly employed and (2) "LAB-6" which has been used for a limited number of tests. Both electrodes are basically the same, but the "LAB-6" has a finer collector grid and less platinum than the "LAB-40".

American Cyanamid electrodes may be obtained with a variety of backing materials. Early "LAB-40" electrodes had a backing designated as "A-2". Recent electrodes have a "B-II-4" backing. The "LAB-6" electrodes have had a type "C" backing. Aside from the fact that these backings are porous and hydrophobic in character, the backing composition has not been divulged. Both electrodes should be resistant to damage from oxygen evolution during the charging cycle, eliminating the need for a third or charging electrode.

2. Cadmium Electrode

The cadmium electrode used in the present unit cells are those developed within Union Carbide as a negative electrode for the nickel-cadmium battery system[1]. It consists of electrochemically deposited cadmium on a nickel screen, pressed to a desired thickness. These electrodes have been plated on a screen or mesh base of copper, silver, or other materials as well as nickel. Single, double and triple layers of standard thickness electrodes have been used to increase unit cell capacities as shown in Table I.

TABLE I.

CAPACITY INCREASE WITH CADMIUM WEIGHT INCREASE

Layer of Std. Stock	Cd-Weight lb.	Component[1] Weight (lb)	Cd-Thickness (in)	Amp-Hrs Capacity	Watt-Hrs/lb Capacity
1	0.0173	0.149	0.022	1.72	8.76
2	0.0340	0.176	0.040	3.00	11.90
3	0.0523	0.185	0.064	4.98	16.20

(1) Includes weight of anode, cathode and electrolyte.

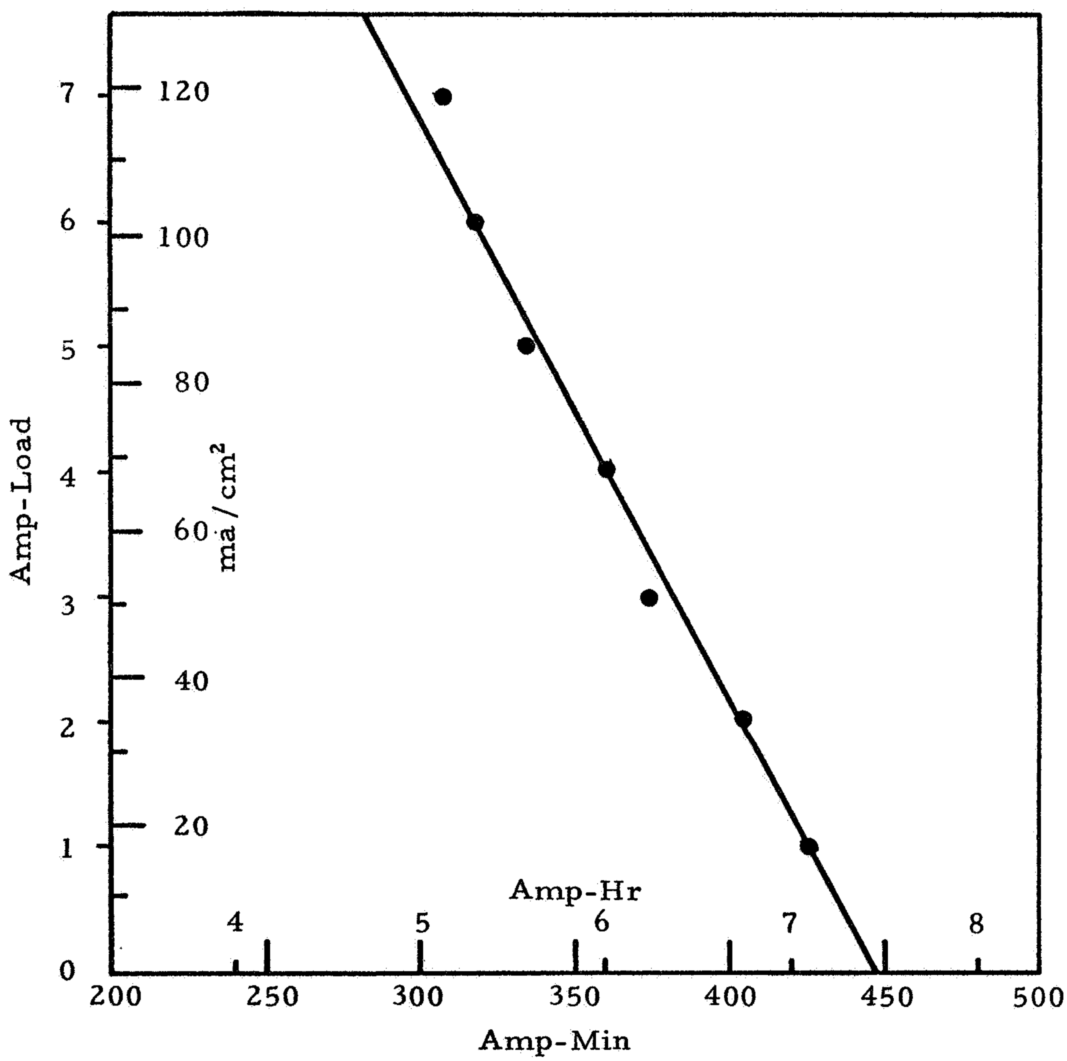
Several cadmium electrodes have been plated with more than the normal amount of cadmium. The heaviest electrode made to date has had an initial capacity of 0.78 amp-hr/in^2 (0.12 amp-hr/cm^2). This electrode plated on a copper mesh has been tested at various rates up to the one-hour rate against a Union Carbide T-2 cathode. In Figure 2 the amp-hr capacity is plotted against current density for the fresh electrode. The test schedule was run through from low current density to high current density and back to low current density where results were within 0.1 amp-hr of the original value.

In all experiments to determine the charge acceptance of these anodes, it has been found that less than 5% overcharge is necessary to completely charge the anode. The only exception has been in the case of cells where electrolyte has been limited to the amount held by capillary action in the pores of the anode and separator. In this case, chemical attack by gaseous oxygen probably occurs reducing the anode capacity and apparent charge acceptance. About 20% overcharge is needed for "wick-type" cells.

FIGURE 2.

CADMIUM-OXYGEN CELL WITH
HEAVY CADMIUM ELECTRODE AT VARIOUS RATES

3" x 3" x 0.085"



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3. Electrolyte

The electrolyte used during the first quarter of the contract period was 33 per cent by weight KOH. At present the concentration is 40 per cent by weight KOH. All electrolyte concentrations were prepared from reagent grade pellets. The electrolyte concentration was changed because it was felt that the higher viscosity solution would help decrease cathode wetting.

4. Separators and Spacers

PELLON No. 10194C and No. 2505W have been used to wrap the cadmium electrode and serve as an anode separator. The 2505W is a tighter felt than the 10194C and is better at inhibiting dendrite growth. A woven polypropylene material known as No. S/700 "waffle weave" obtained from the Lamports Co. has been used to provide spacing between the electrodes. Another polypropylene screen-like material, known as "onion bag material", is available from Vexar Sabo Division of E. I. DuPont de Nemours Co. as 30 PDS 89. An expanded TEFLON, 20-TEFLON-25-1, spacer may be used in place of the "waffle weave" with excellent results. This material was obtained from Exmet Corp.

When a separate charging electrode is used, its separation from the anode may be obtained by heat fusing thin plastic ribs to the charging electrode. These serve to provide a free gas escape path, help support the anode, and give uniform spacing.

5. Cathode Current Collector and/or Gas Space Support

The Union Carbide electrode is capable of serving as its own current collector at low current densities due to the porous metal backing. It is, however, a very thin and flexible electrode and needs support on the gas side to prevent collapse into the space provided for oxygen circulation. Adequate support and enhanced current collection are obtained by the use of an expanded nickel grid in the gas space. Material designated as 5 Ni 15-2/0 obtained from Exmet Corporation has been used for this purpose.

The American Cyanamid electrodes are capable of serving as their own current collectors because of the embedded gold-plated nickel screen. Both electrodes are also quite rigid with the "LAB-40", more rigid than the

"LAB-6". In small test cells, the "LAB-40" needs no support on the gas side, and the "LAB-6" needs only a few isolated support points. In projecting cell sizes to larger capacity, a gas space support will be needed for either type of electrode chosen. The expanded TEFLON sheet listed with the separators above may be used for this purpose.

B. Experimental Unit Cell Construction

1. Three-Electrode System

As mentioned in describing the Union Carbide T-2 cathode, it is necessary to provide a third electrode so that the cell cathode may be left idle while charging the cadmium electrode and generating oxygen on the third electrode. Several variations in cell construction were made and tested. Initially, the charging electrode was placed between the anode and cathode with S/7700 polypropylene mats on each side of the charging electrode. With this arrangement the anode-to-cathode spacing was greater than one quater of an inch, and internal resistance on discharge was high. The operating characteristics of such a cell are depicted by Cell No. 21 in Table II.

The most important modifications involved moving the charging electrode to the other side or back of the anode. This change provides for closer anode-to-cathode spacing with resulting high discharge voltage, and removal of one of the thick polypropylene mats with a reduction of required electrolyte. This results in higher power density because of higher voltage and lower weight. Test results have shown that the type of anode used can be charged efficiently and completely from the back for anodes at least 0.085 inch thick. Operating characteristics of this type cell are shown by Cell No. 16 in Table II.

A further reduction in electrolyte volume was obtained by replacing the one remaining polypropylene mat between the charging electrode and the anode with narrow plastic ribs fused onto the charging electrode. It was also found satisfactory to place the charging electrode against the PELLON separator covering the anode, with the plastic ribs extending outward from the opposite side of the charging electrode. The ribs provide a gas escape path and we have been unable to detect any reduction in charging efficiency which might be due to oxygen gas migrating through the separator and chemically discharging the anode. This construction is shown in Figure 3. Characteristics of such a cell are given by Cell No. GL-1 in Table II.

TABLE II.

COMPARISON OF CONSTRUCTION VARIATIONS IN THREE-ELECTRODE SYSTEMS

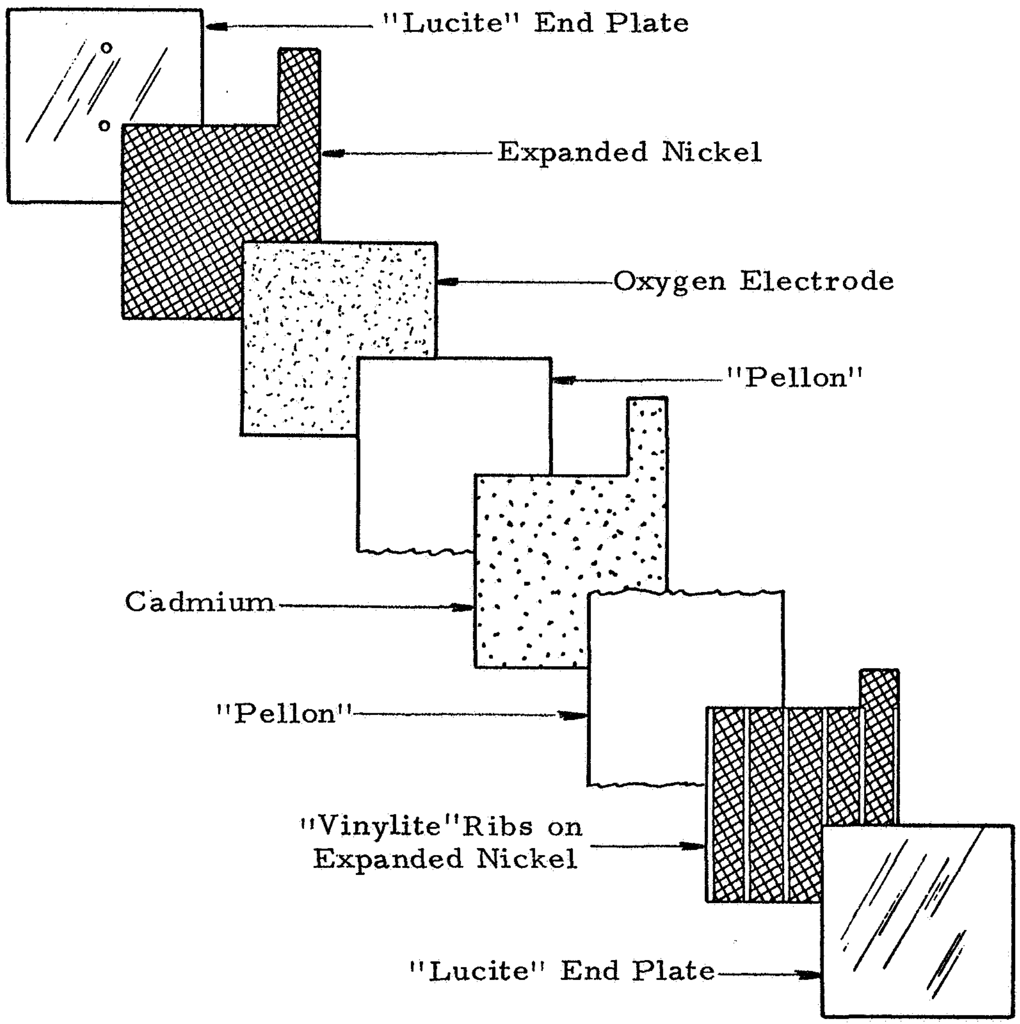
Performance Data Is Average of All Cycles Completed

Variation	Cell No. 21 Standard Construction (O_2-Ni-Cd)	Cell No. 16 Charging electrode behind Cadmium	GL-1 Prototype Cell
Cd Weight (lb.)	0.0186	0.0186	0.033
Component Weight[1] (lb)	0.168	0.151	0.109
Average Input (Ampere-Hours)	1.66	1.84	1.88
Average Output (Ampere-Hours)	1.64	1.69	1.85
Average Discharge Voltage (Volts)	0.79	0.81	0.82
Average Component Capacity (Watt-Hours per pound)	7.70	9.07	13.90
Average Current Density (ma/cm^2)	13.80	14.85	17.70

[1] Components consist of oxygen electrode, electrolyte, cadmium electrode and charging electrode.

FIGURE 3.

DETACHED VIEW OF THREE-ELECTRODE UNIT CELL AS REDESIGNED



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The components of the three-electrode unit cell are given in Table III. The table lists the component description and source of supply It also lists dimensions and weights in a typical test cell.

TABLE III.

COMPONENTS OF THE THREE-ELECTRODE UNIT CELL

Component	Dimensions	Weight
1) Cathode Collector - Expanded Nickel Exmet Corp. 5 Ni 15 2/0	3 x 3 x 0.025 in.	2.0 g
2) Cathode - Oxygen "Fixed Zone" Union Carbide Corp. Type 2	3 x 3 x 0.022 in.	9.0 g
3) Anode Separator - Nylon Felt Pellon Corp. No. 10194C or 2505W	28 sq. in.	1.2 g
4) Anode - Cadmium on Ni Screen Union Carbide Corp. Electrodeposited	3 x 3 x 0.030 in.	13.5 g
5) Charging Electrode - Expanded Nickel Exmet Corp. 5 Ni 15 2/0 with Plastic Ribs, Union Carbide Corp. Rigid "Vinylite" 0.025 in. thick	3 x 3 x 0.060 in. (incl. ribs)	3.7 g
6) Electrolyte - 40% KOH Reagent Grade	approx. 20 ml Sp. g. 1.40	28.0 g
7) Oxygen - Commercial Cylinder	0.298 g/amp-hr	0.6 g

2. Two-Electrode System

The American Cyanamid "LAB-40" and "LAB-6" electrodes may be used both as the cell cathode on discharge and as the charging electrode. Initially a cell was made with the same interelectrode spacing as that used for the earlier three-electrode unit cells. This called for the use of two S/7700 polypropylene spacers between the anode and the cathode. Very poor cell characteristics were obtained as shown by Cell No. 20 in Table IV.

TABLE IV.

COMPARISON OF CONSTRUCTION VARIATIONS IN THE TWO-ELECTRODE SYSTEM

Performance Data Is Average of All Cycles Completed

Variation	Cell No. 20 2 polypropylene spacers between electrodes	Cell No. 32 1 polypropylene spacer between electrodes	Cell No. GL-4 Prototype Cell
Cd Weight (lb)	0.0192	0.021	0.033
Component Wt.[1] (lb)	0.152	0.113	0.103
Average Input (Ampere-Hours)	1.08	1.87	1.96
Average Discharge Voltage (Volts)	0.83	0.84	0.84
Average Output (Ampere-Hours)	1.05	1.78	1.77
Average Component Capacity (Watt-Hours per pound)	5.74	13.22	14.42
Average Current Density (ma/cm^2)	17.5	16.0	18.1

(1) Components consist of oxygen electrode, electrolyte, cadmium electrode.

The construction was modified to use one 30 PDS 89 polypropylene spacer between the anode and cathode with greatly improved cell performance as shown by Cell No. 32 in Table IV. It was observed that most of the oxygen generated during charging is evolved from the gas side of the "LAB-40" and "LAB-6" electrodes. It was therefore possible to further reduce the anode to cathode spacing by dispensing with the spacer altogether. The operating characteristics of a cell reduced to the minimum electrolyte space and representative of the contract effort is given by Cell No. GL-4 in Table IV.

The components of the cell depicted in Figure 4. are listed in Table V. Descriptions and sources of supply are given as well as sizes and weights.

C. Unit Cell Performance

1. Three-Electrode System

Unit cells have been tested at several charge/discharge regimes at ambient temperature, and at 0° C and 40° C on the two-hour charge/two-hour discharge regime. Originally our high rate charge/low rate discharge, and low rate charge/high rate discharge tests were set up on a two-hour/twenty-four hour ratio. This was later changed to a two-hour/twenty-two hour ratio to fit into a daily twenty-four hour schedule. Results have shown no detectable difference between the two-hour/twenty-four hour and the two-hour/twenty-two hour schedule, and data will be coordinated and reported as a two-hour/twenty-two hour or twenty-two hour/two-hour schedule. Typical cell test results are given in Table VI. In general, these are not the best or the worst tests of a category, but are tests which are typical of the charge/discharge regime they are depicting.

All tests cycled on the one-hour charge/one-hour discharge regime at 40 ma/cm^2 discharge current density were small cells with only 6.45 cm^2 of anode area. The cell structure was that of Figure 3. with a double layer of PELLON separator on both sides of the anode. Test results were terminated because of mechanical trouble in the cycling apparatus rather than cell failure. The cells were still operating at 70% of their original capacity after 384 cycles. Typical charge and discharge cycles are shown in Figure 5.

So much of the testing has been done on the two-hour charge/two-hour discharge that two examples of "typical" cells are given in Table VI. The first

FIGURE 4.

DETACHED VIEW OF TWO-ELECTRODE UNIT CELL

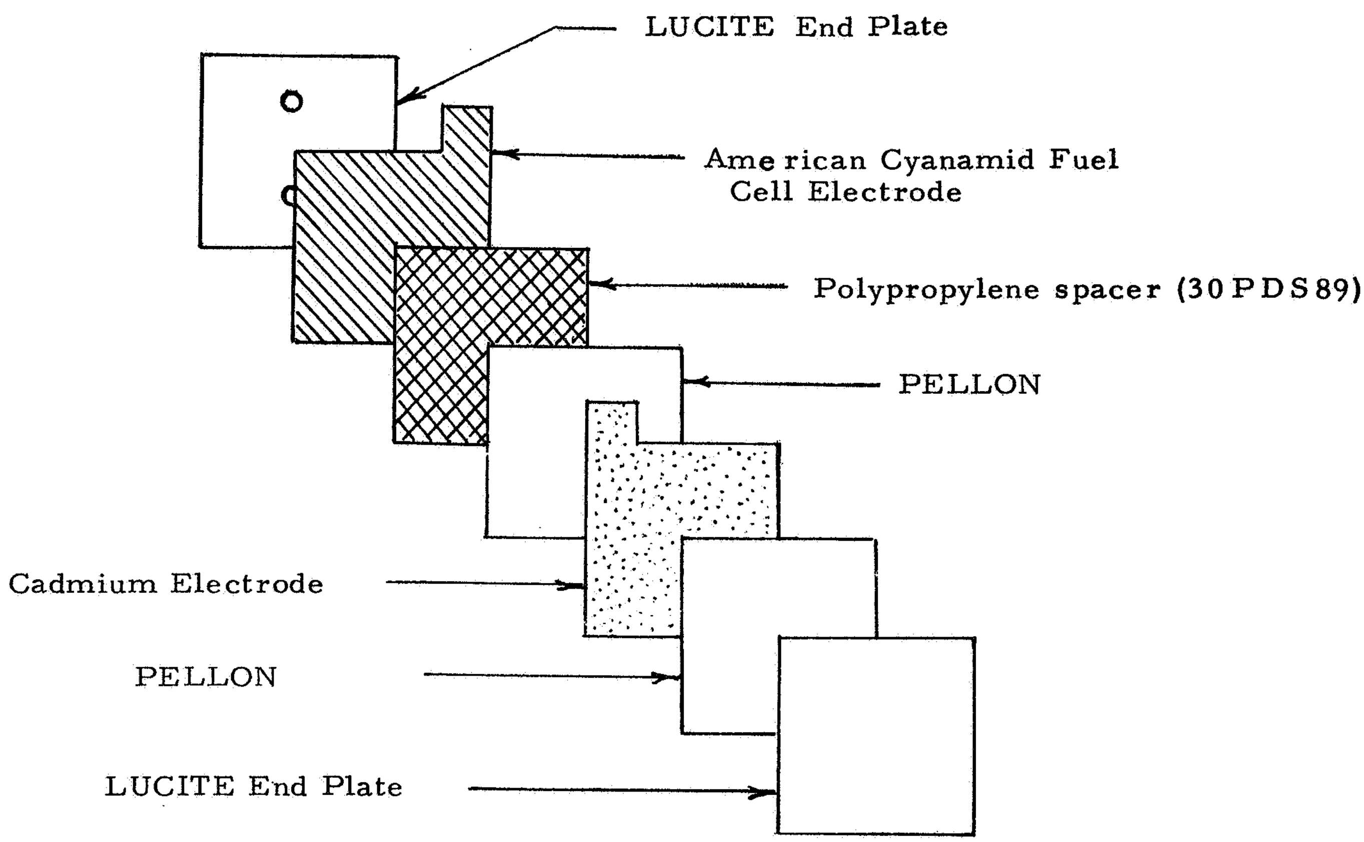

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TABLE V.

COMPONENTS OF THE TWO-ELECTRODE UNIT CELL

Component	Dimensions	Weight
1. Cathode - Oxygen American Cyanamid LAB-40	3" x 3" x 0.28"	15.0 g
2. Anode Separator - Nylon Felt Pellon Corp. No. 10194C or 2505W	28 sq. in.	1.2 g
3. Electrode Spacer - Polypropylene Vexar Sabo Div., DuPont 30 PDS89	3" x 3" x 0.045"	1.5 g
4. Anode - Cadmium on Nickel Screen Union Carbide Corp. - Electrodeposited	3" x 3" x 0.030"	13.5 g
5. Electrolyte: 40% KOH; Reagent Grade	15 ml Sp. g. 1.40	21.3 g
6. Oxygen - Commercial Cylinder	0.298 g/amp-hr	0.6 g
		53.1 g

TABLE VI.

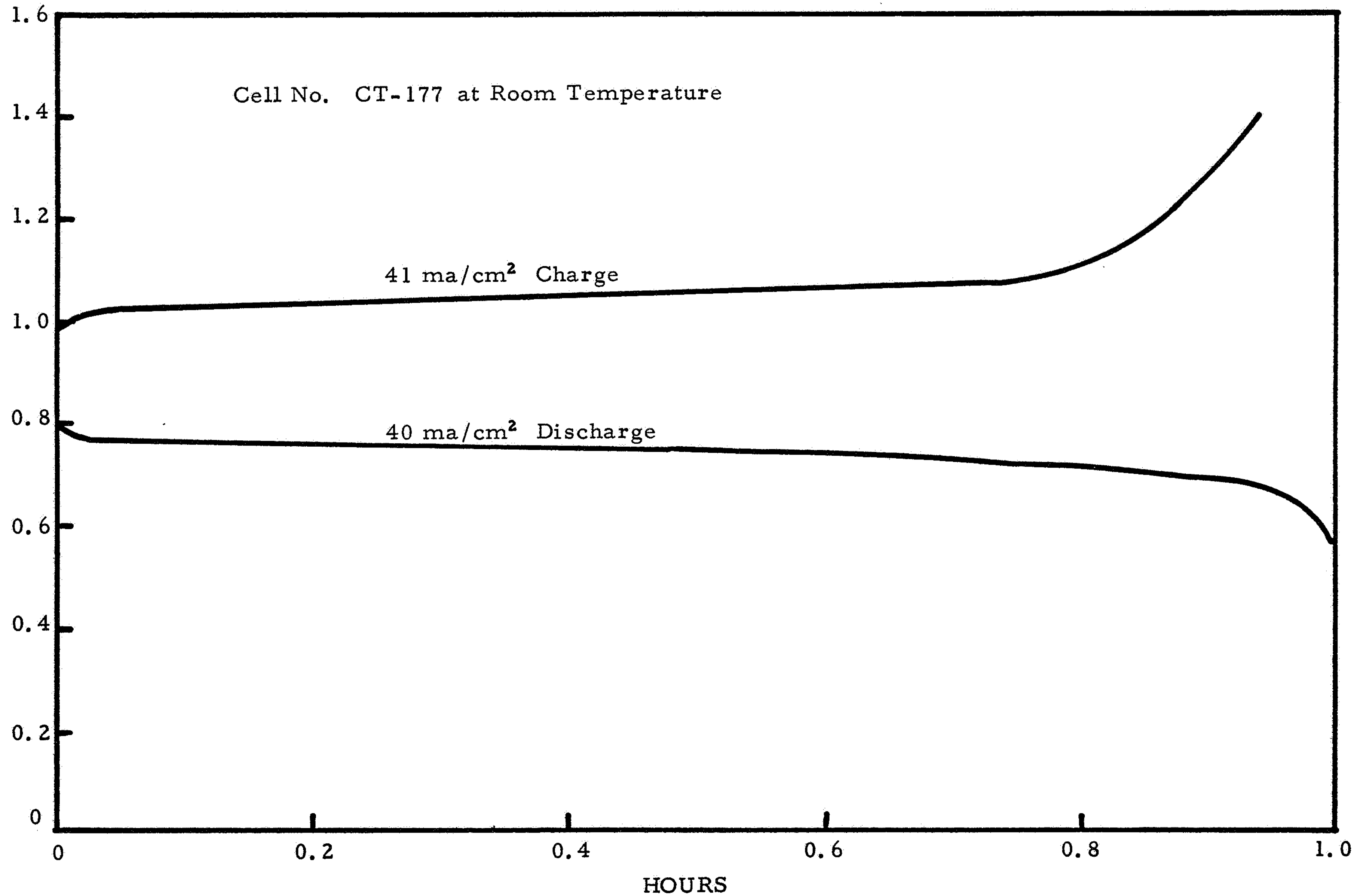
TYPICAL ROOM TEMPERATURE PERFORMANCE OF THREE-ELECTRODE CELLS AT VARIOUS CHARGE/DISCHARGE REGIMES

Chge/Dischge Regime & Anode Area	Cycle	Input Amp-Hr	Discharge Volts	Discharge ma/cm²	Output Amp-Hr	Watt-Hr/lb (Excluding Case)
1 hr/1 hr	3	0.23	0.708	40	0.24	11.0
6.45 cm²area	10	0.25	0.710	40	0.24	11.1
	50	0.22	0.740	40	0.22	10.6
Cell No CC-177	100	0.23	0.710	40	0.22	10.1
	200	0.18	0.721	40	0.18	8.4
	300	0.18	0.714	40	0.18	8.3
	384	0.17	0.714	40	0.17	7:9
			******************			
2 hr/2 hr	3	2.17	0.740	15.5	1.75	7.7
58 cm² area	21	----	0.740	17.3	1.97	8.6
	43	----	0.720	16.5	1.71	7.3
Cell No. 3	153	1.70	0.750	17.2	1.62	7.2
	203	1.68	0.780	14.9	1.68	7.8
	306	1.50	0.780	15.1	1.46	6.8
	394	1.32	0.710	13.8	1.36	5.7
	503	0.95	0.700	13.3	0.90	4.1
			******************			
2 hr/2 hr	7	2.00	0.800	17.2	2.00	14.1
58 cm² area	13	2.00	0.810	17.0	1.92	13.7
	47	1.92	0.820	16.8	2.05	14.9
Cell GL-1	111	1.77	0.825	17.2	1.73	12.6
	215	2.00	0.820	17.2	1.68	12.2
	307	2.00	0.820	17.2	1.32	9.6
			******************			
2 hr/22 hr	1*	1.56	0.760	15.2	1.26	5.7
58 cm² area	16	2.25	0.900	1.7	1.98	10.6
	21	2.00	0.890	1.4	1.85	9.8
Cell No. 47	26**	1.95	0.890	1.4	1.82	9.6
* 2 hour charge/2 hour discharge break-in regime for 15 cycles.						
** No cells left on this regime for total life.						
			******************			
22 hr/2 hr	3	2.14	0.77	14.7	2.01	9.9
58 cm² area	10	1.95	0.79	13.8	1.83	9.3
	50	1.80	0.80	13.8	1.35	6.9
Cell No. 57	77	1.80	0.82	13.8	1.32	7.0
			******************			
24 hr/24 hr	3	2.18	0.85	1.6	2.11	9.8
58 cm² area	11	2.18	0.86	1.6	1.95	9.1
	30	1.94	0.91	1.4	1.82	9.0
Cell No. 30	53	1.46	0.88	1.0	1.36	6.5
	54	1.46	0.76	13.8*	0.91	3.8

* Last cycle at 2 hour rate.

FIGURE 5.

TYPICAL CHARGE & DISCHARGE CURVE OF 0.25 AMP-HR CELL AT THE ONE-HOUR RATE



C-4212

is representative of the early work with the charging electrode between the anode and cathode and thick S/7700 polypropylene spacers separating the electrodes. The second example is more representative of the cell construction of Figure 3. and of the prototype cells constructed for delivery under the contract. Note that the newer construction operates at higher average discharge voltage and has a much higher power density due to the increased voltage and decreased volume of electrolyte. Typical charge and discharge cycles for this charge/discharge regime are shown in Figure 6. for Cell No. 21 while it was on this regime.

No cells were run for total cycle life at the two-hour charge/twenty-two-hour discharge (or twenty-four-hour discharge). However, sufficient testing was done to characterize the system. These tests were made with cells of the earlier construction where the charging electrode is between the anode and cathode, and thick S/7700 polypropylene spacers were used. Cell No. 47 (Table VI) was placed on this regime for cycles 16 through 26, and its performance checked early in cell life. A second cell, No. 21, was changed to this regime for cycles 133 through 151 where its performance was observed as a cell late in life. A charge/discharge cycle for cell No. 47 is shown in Figure 7.

Results of a more recent test (Cell No. 57) with the new construction (Figure 3) are available on twenty-two-hour charge/two-hour discharge. This cell test was terminated because an apparent short between the anode and charging electrode prevented charge acceptance. A typical charge and discharge curve for this cell is shown in Figure 8.

The twenty-four-hour charge/twenty-four-hour discharge tests were all made with the early cell structure. Assuming at least equivalent voltage characteristics for the newer cell structure, the reduced component weight would result in a power density value of 16 watt-hr/lb at 1.5 ma/cm^2. Typical curves for Cell No. 30 are shown in Figure 9.

A plot of voltage and power density versus current density, as given in Figure 10, generally characterizes the system. These curves are based on the results quoted in Table VI and simple extrapolations as discussed in

FIGURE 6.

INITIAL PERFORMANCE OF CELL No. 21 AT 25°C
Charge 15.5 ma/cm² - Discharge 13.8 ma/cm²

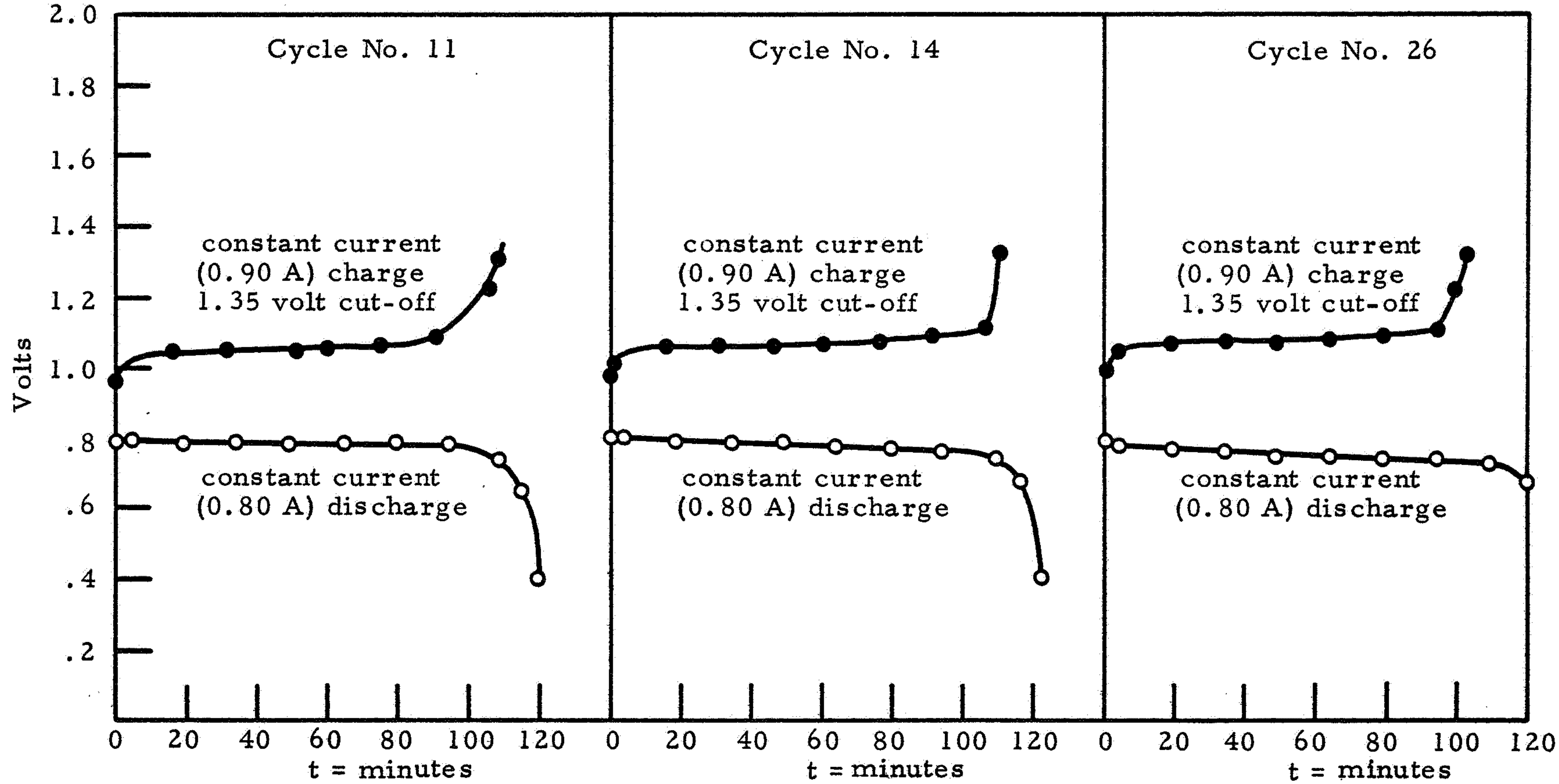


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FIGURE 7.

CHARACTERISTIC CHARGE AND DISCHARGE CURVES FOR CELL No. 47
ON THE TWO-HOUR CHARGE/24-HOUR DISCHARGE REGIME

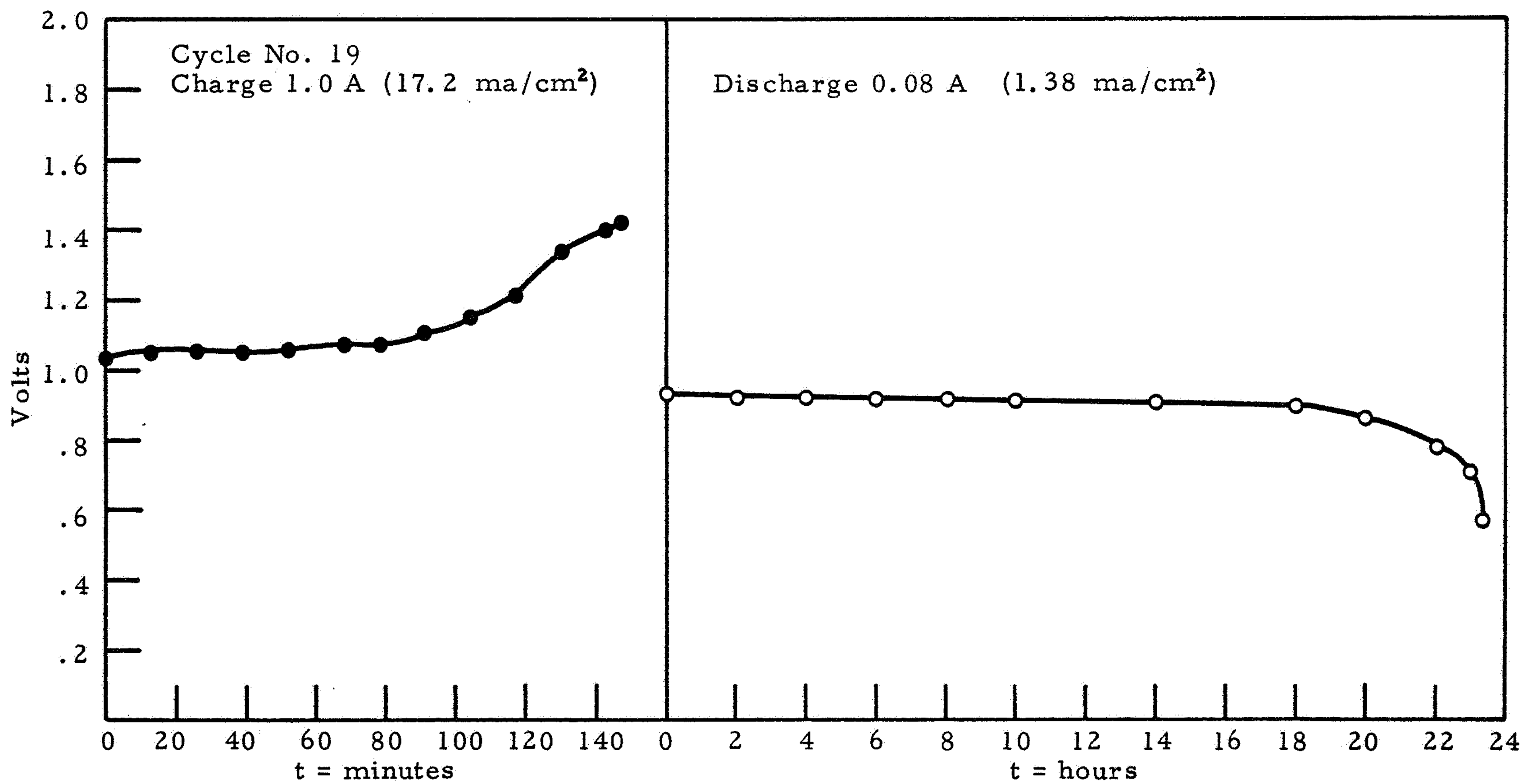

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FIGURE 8.

CHARACTERISTIC CHARGE AND DISCHARGE CURVES FOR CELL NO. 57 ON 22-HOUR CHARGE/2-HOUR DISCHARGE REGIME

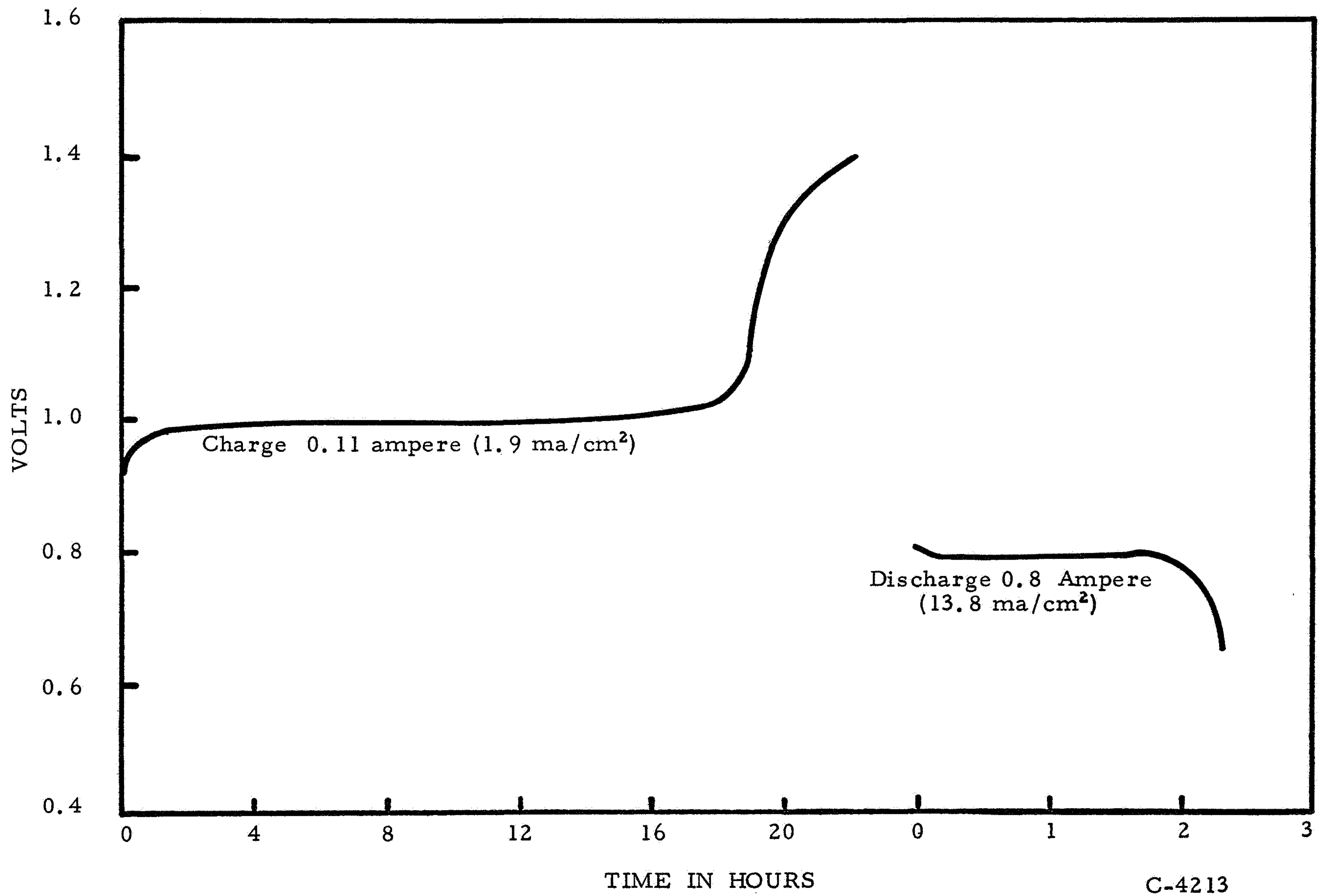
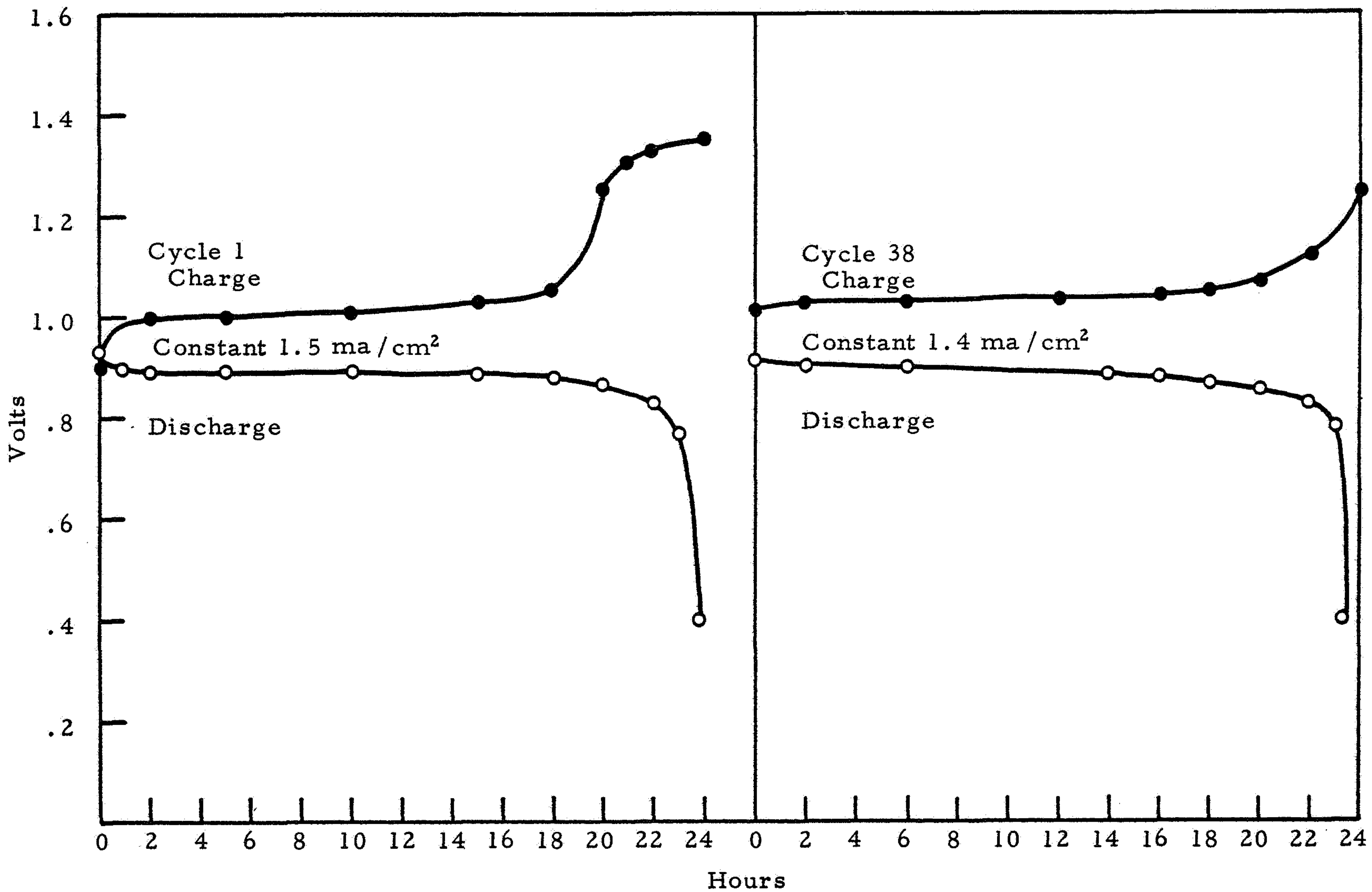


FIGURE 9.

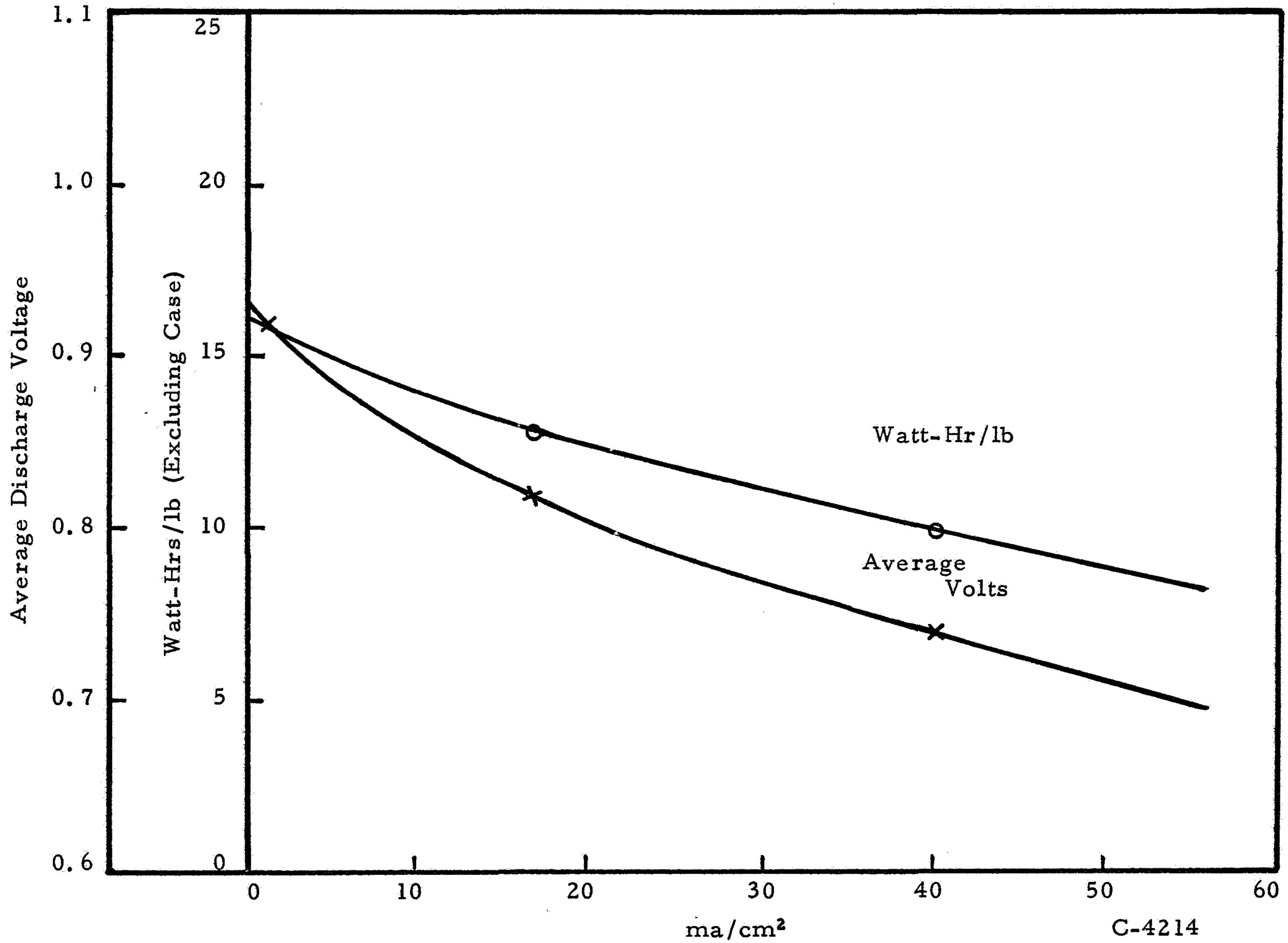
CHARACTERISTIC CHARGE AND DISCHARGE CURVES FOR CELL No. 30 ON THE 24-HOUR CHARGE/24-HOUR DISCHARGE REGIME



C-3949

FIGURE 10.

ROOM TEMPERATURE CELL CHARACTERISTICS OF THE THREE-ELECTRODE SYSTEM AFTER 100 HOURS OF OPERATION, BASED ON MOST RECENT CELL STRUCTURES



C-4214

the preceding paragraph. Cycle life is not as easily predicted. Results to date have shown the cathode to be the limiting electrode due to a slow loss of electrolyte repellency. It has been found that a total service life (prior to leakage) of from 2,000 to 3,000 hours is normal for the T-2 electrode, essentially independent of the load. Provisions for removing and replenishing the leaking electrolyte and operation at reduced capacity will permit much greater cycle life.

Extrapolation of the power density which will result from increasing the cell capacity can be made from the data of Figure 5. Assuming full 2.0 amp-hr capacity in a fresh cell operating at these voltages and using typical weights from recently tested cells, a standard curve can be derived for current density versus power density. If the cell capacity is increased by doubling the capacity of the anode to 4.0 amp-hr, the cell is made a little thicker and the electrolyte capacity is increased by the volume of the anode pores (about 30% of anode volume). The anode is now 0.060 inch thick, doubling it again would make it about 0.120 inch thick. It is felt that anodes this thick are approaching the limit of reasonable efficiency based on present experience, and represent an arbitrary upper limit of power density for a simple three-electrode cell. However, by placing anodes connected in parallel on each side of a single charging electrode and using two cathodes, there are some additional weight gains which increase the power density again. Thus, a cell with two cathodes, two anodes 0.120 inch thick, one charging electrode would have the maximum capacity when limited to this anode thickness. A summary of calculations based on these extrapolations are given in Table VII. and the power density is plotted in Figure 11.

From these calculations it can be seen that simply increasing the anode capacity increases the power density most rapidly up to the limit of anode capacity. However, the dual electrode structure with a single charging electrode offers the maximum power density for a given anode capacity limit.

All of the tests discussed so far have been run at ambient temperature (25° ± 3° C). A number of tests have been made at 40° C and at 0° C at the two-hour charge/two-hour discharge rate. The test results at 40° C have shown more severe degradation of the cathode with cycle life than was found at room temperature. This has been attributed to more rapid wetting of the

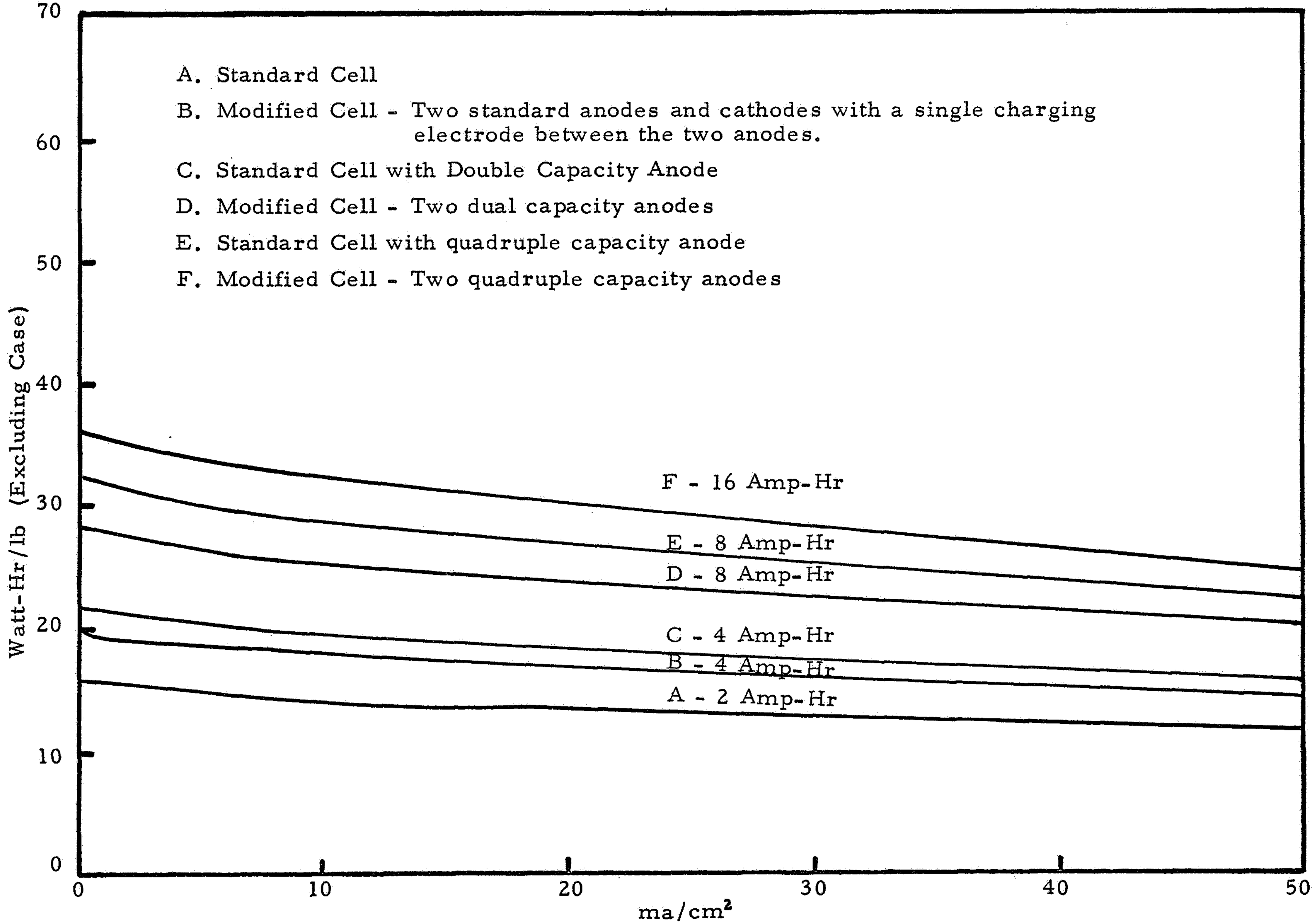
TABLE VII.

EXTRAPOLATION OF POWER DENSITY FOR HIGHER CAPACITY CELLS
FOR THE THREE-ELECTRODE SYSTEM (3" x 3" Cell Excluding Case)

Components	Component Weights for Extrapolation					
	Fig. 3 Standard Cell (grams)	Double Capacity Anode (grams)	Two Single Anodes and Cathodes (grams)	Quadruple Anode (grams)	Two Double Anodes and Two Cathodes (grams)	Two Quadruple Anodes and Two Cathodes (grams)
Anode & Lead	15.70	30.70	30.70	60.70	60.70	120.70
Cathode & Lead	12.15	12.15	23.60	12.15	23.60	23.60
Chg. Electrode & Lead	3.73	3.73	3.73	3.73	3.73	3.73
Separator	1.20	1.20	2.40	1.20	2.40	2.40
Cathode Support (Gas Space)	1.93	1.93	3.86	1.93	3.86	3.86
Electrolyte	19.60	21.00	22.80	23.50	25.60	31.20
Total Wt. (grams)	54.31	70.71	87.09	103.21	119.89	185.49
Total Wt. (lbs.)	0.1195	0.1715	0.1920	0.2270	0.2640	0.4080
Capacity (Amp-Hr)	2.0	4.0	4.0	8.0	8.0	16.0
Expected Voltage at:						
1.5 ma/cm^2	0.92 v	0.91 v	0.92 v	0.90 v	0.91 v	0.90 v
17.0 ma/cm^2	0.82 v	0.80 v	0.82 v	0.78 v	0.80 v	0.78 v
40.0 ma/cm^2	0.74 v	0.71 v	0.74 v	0.68 v	0.71 v	0.68 v
Watt-Hr/lb at:						
1.5 ma/cm^2	15.4	21.2	19.2	31.7	27.6	35.3
17.0 ma/cm^2	13.7	18.7	17.1	27.5	24.2	30.6
40.0 ma/cm^2	12.4	16.5	15.4	24.0	21.5	26.6

FIGURE 11.

EXTRAPOLATION OF POWER DENSITY FOR HIGHER CAPACITY CELLS, THREE-ELECTRODE SYSTEM
3" x 3" CELLS



C-4215

cathode at the elevated temperature. Cycle life has ranged from 100 to 250 cycles at this temperature as compared to 200 to 600 cycles at 25° C. Typical charge and discharge curves are shown in Figure 12 for Cell No. 21. This cell has been tested at all three temperatures for purposes of comparison (See Figures 6 and 13).

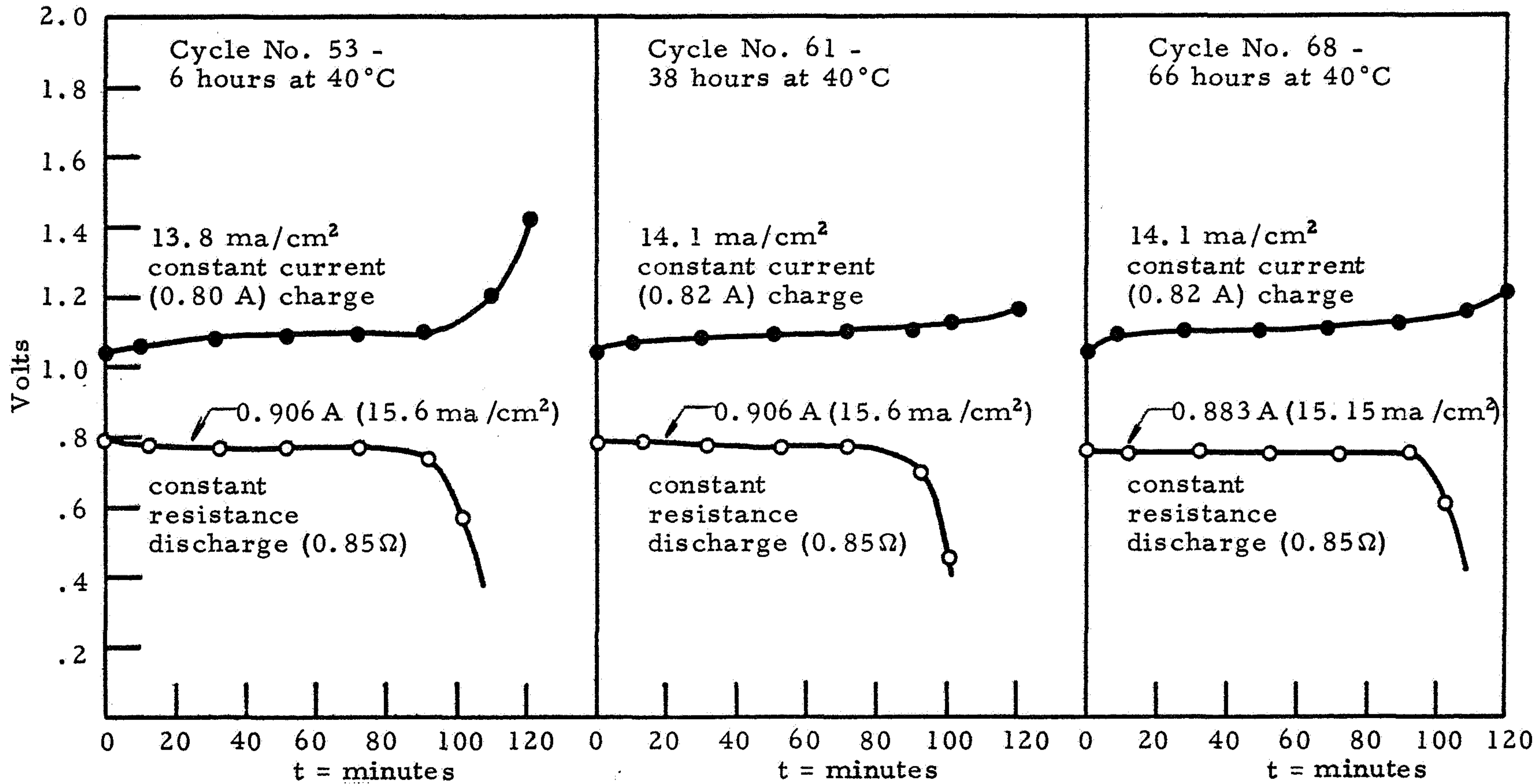
At 0° C the cycle life has been found to be greatly reduced to from 20 to 90 cycles because of cathode polarization. Usually cells which have failed at 0° C will, after warming to room temperature, give nearly normal performance. The cause of failure is attributed to precipitation of KOH crystals in the pore structure of the cathode. Typical curves for Cell No. 21 are given in Figure 13.

A few cells have been operated within an enclosed container so that the cell generated an oxygen pressure on charge and consumed the oxygen on discharge. These cells have been of a somewhat different construction in that the cells are not flooded with electrolyte, but filled only with the amount of electrolyte which can be held in the cells by capillary action. At the start of a test, the cell container is flushed with oxygen then charged with oxygen to about 10 psi. The free space in the container is about 190 ml. The charging current is then started and the oxygen pressure builds up to about 25 to 27 psi at the end of charge. During discharge the oxygen pressure drops again to about 10 psi at the end of discharge. In order to accommodate a small amount of overcharge, a platinum catalyzed "getter" was placed inside the container to act as an oxygen-hydrogen recombination catalyst. There has been no excessive pressure build up during overcharge with this precaution.

The first two cells of three tested inside an oxygen container were made with asbestos separators because of its excellent wicking capability. It was soon discovered that something in the asbestos was poisoning the cadmium anode and rapidly reducing its capacity. Cellulosic separators, although excellent wicks, are readily oxidized. As an expedient, a third cell was constructed using porous nickel wicks and PELLON insulating separators. Initial tests of this cell were conducted on a four-hour charge/four-hour discharge cycle at current densities of 8.9 ma/cm^2 (350 ma) and 7.6 ma/cm^2 (300 ma) respectively. After twenty-eight cycles the regime was changed to a two-hour

FIGURE 12.

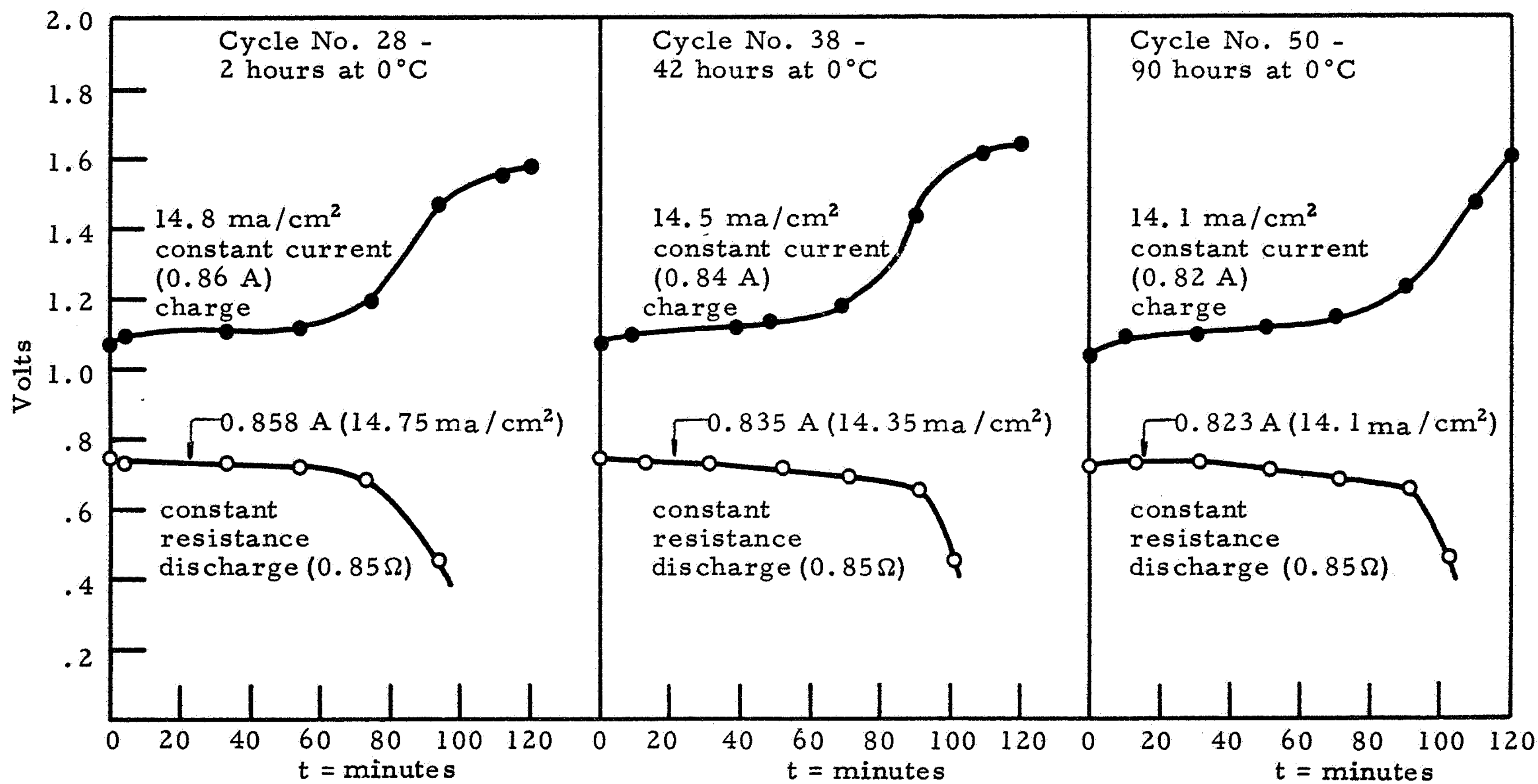
PERFORMANCE OF CELL No. 21 AT 40°C



C-3951

FIGURE 13.

PERFORMANCE OF CELL No. 21 AT 0°C



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charge at 17.7 ma/cm^2 (700 ma) and a two-hour discharge at 15.2 ma/cm^2 (600 ma). There is apparently some access of oxygen to the anode as charging efficiency goes up with increased charging rate. A total of 34 cycles have been completed to date and the cell is continuing to cycle. A typical charge/discharge curve is shown in Figure 14. Included is a plot of oxygen pressure versus time for one complete cycle for this particular cell.

2. Two-Electrode System

Unit cells having the structural configuration of Figure 4 and utilizing the American Cyanamid LAB-40 cathode have been tested at the three temperatures used in testing the three-electrode system and on most of the same charge/discharge regimes. No tests were made in the small one square inch area cell at the one-hour rate. All other test schedules were used.

In this cell structure, the cathode is also the limiting electrode. The first electrode obtained had a backing designated as "Type A-2" by American Cyanamid. The electrodes allowed oxygen to bubble through if a pressure of more than about two inches of water was used. On the other hand without at least this much gas pressure, electrolyte leakage occurred quickly. A second group of electrodes with a "Type B-II-4" backing have been much improved in this respect. Wherever possible, data for system characterization will be taken from cells using the LAB-40 electrode with B-II-4 backing.

Typical room temperature cell performance for two-electrode cells using LAB-40 electrodes is given in Table VIII. Cell No. 35 and Cell No. 70 give a comparison of early cells with large electrolyte spaces and cathodes with Type A-2 backing (Cell No. 35) with later (Figure 4) cells having lower electrolyte volume requirements and cathodes with Type B-II-4 backing on the two-hour charge/two-hour discharge regime. There has been a general improvement in cycle life as well as marked increase in power. A typical charge/discharge cycle is shown in Figure 15.

Testing on the two-hour charge/twenty-two hour discharge and the twenty-two hour charge/two-hour discharge regimes was not extensive. Sufficient work was done with LAB-40 electrodes in the cell structure of

FIGURE 14.

CADMIUM-OXYGEN RECHARGEABLE CELL IN PRESSURIZED CONTAINER

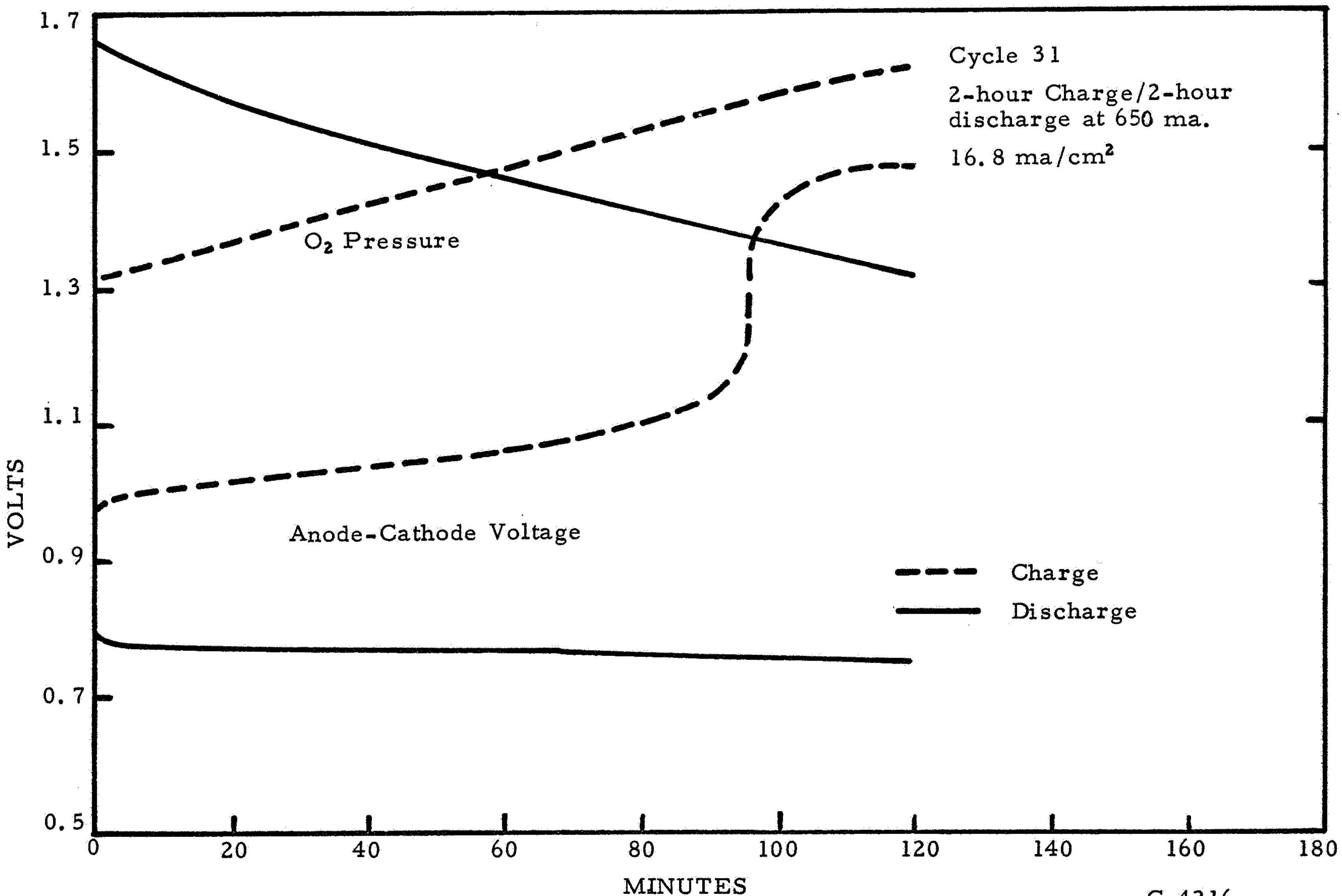

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TABLE VIII.

TYPICAL ROOM TEMPERATURE PERFORMANCE OF TWO-ELECTRODE CELLS AT VARIOUS CHARGE/DISCHARGE REGIMES
(All Cells Have a Working Area of 58 cm^2)

Chge/Dischge Regime	Cycle No.	Input Amp-Hr	Input Cut-off Voltage	Discharge Volts	Discharge ma/cm^2	Output Amp-Hr	Watt-Hr/lb (Excluding Case)
2 hr/2 hr	4	1.32	1.60	0.88	14.2	1.37	7.2
Cell No. 35	28	1.19	1.75	0.85	13.7	1.17	5.9
	52	0.84	1.75	0.80	15.5	0.84	4.0
	185	0.90	1.80	0.77	15.5	0.84	3.9
	210	0.21	1.80	0.76	15.5	0.20	0.9
	270	0.10	1.80	0.78	15.5	0.09	0.4
	340	0.15	1.85	0.76	13.8	0.16	0.7
			******************				
2 hr/2 hr	2	1.80	1.52	0.84	15.5	1.80	11.2
Cell No. 70	12	2.00	1.90	0.83	17.2	2.00	12.3
	45	1.80	1.82	0.82	15.5	1.68	10.2
	100	1.76	1.83	0.81	15.2	1.62	9.7
	190	1.76	2.0+	0.81	15.1	1.76	10.5
	298	1.64	1.80	0.82	14.1	1.56	9.5
	400	1.40	1.80	0.81	12.1	1.20	7.2
	443	1.40	1.80	0.72	12.1	0.47	2.5
			******************				
2 hr/22 hr	2	2.00	1.50	0.90	2.2	2.16	14.0
Cell No. 71	10	2.00	1.93	0.90	1.5	1.96	12.7
	25	2.00	1.93	0.90	1.5	1.96	12.7
	37	2.00	2.00	0.87	1.7	1.87	11.7
	49	2.00	2.00	0.88	2.0	2.06	13.0
	51*	2.00	1.90	0.85	2.1	1.75	10.7
*Case ruptured.			*******************				
22 hr/2 hr	7	2.20	1.50	0.84	15.5	1.80	14.2
Cell No. 68	19	2.20	1.57	0.78	18.6	1.89	14.2
	60	2.20	1.56	0.75	17.2	1.87	13.2
	88*	2.20	1.42	0.77	15.5	1.44	11.5
*Changed to 2 hr/2hr regime after Cycle 88.							
			******************				
24 hr/24 hr	5	1.71	1.74	0.80	12.5	1.40	6.3
Cell No. 25	41	1.30	1.50	0.90	1.55	1.44	7.3
	51	1.92	----	0.91	1.38	1.83	9.4
	67	1.92	----	0.87	1.38	1.80	8.8
	81	1.87	1.66	0.88	1.34	1.59	7.9
	98	1.87	1.50	0.89	1.34	1.61	8.0

FIGURE 15.

CHARACTERISTIC CHARGE AND DISCHARGE CURVES FOR THE TWO-ELECTRODE SYSTEM ON 2-HR. REGIME

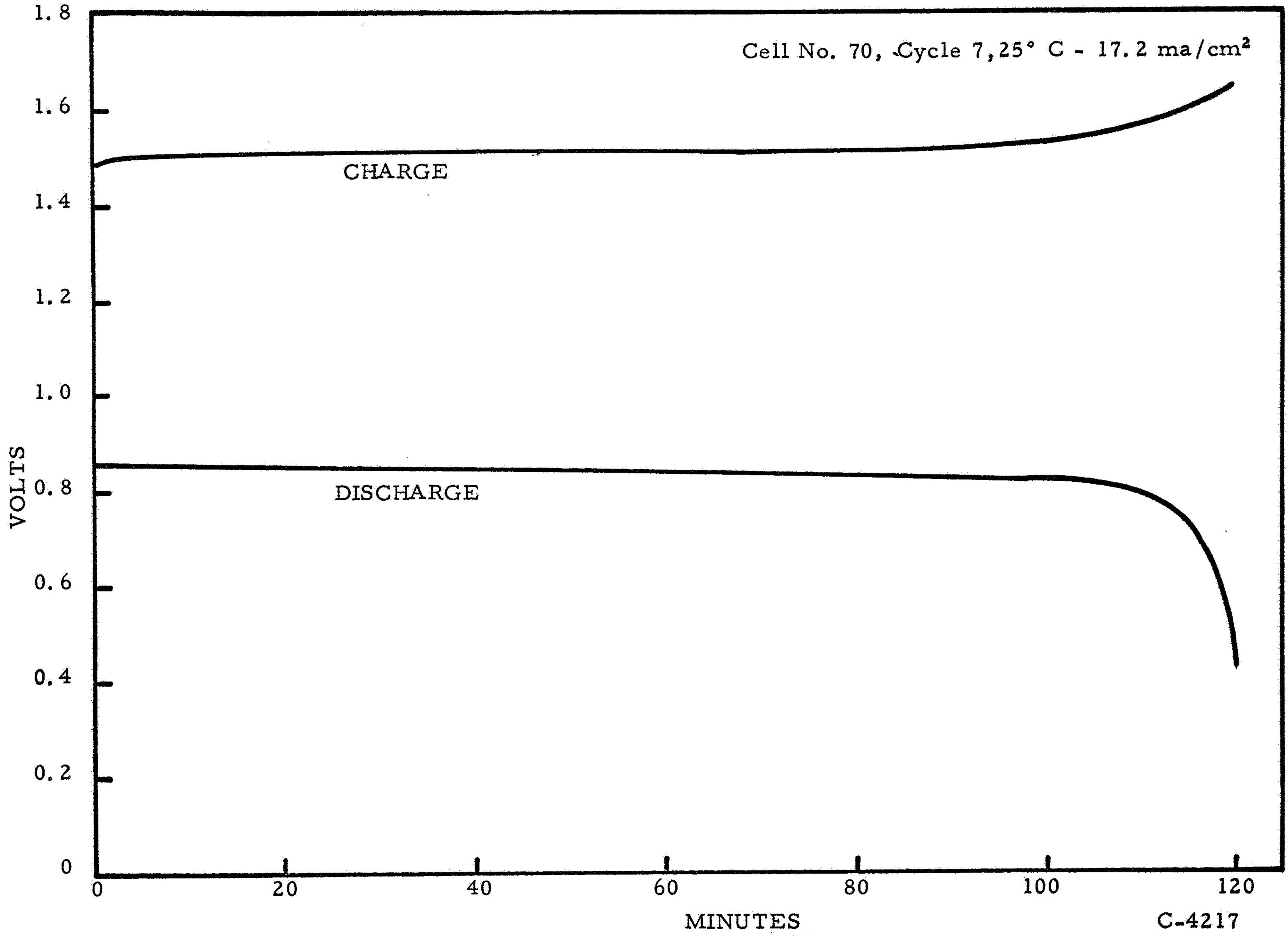


Figure 4. to show cell characteristics, but cycle life data are limited. Representative charge/discharge curves for these regimes are shown in Figures 16 and 17.

The test results for the twenty-four hour charge/twenty-four hour discharge regime were obtained with an early cell structure with excess electrolyte space and the older LAB-40 with type A-2 backing. Voltage characteristics on charge and discharge are shown in Figure 18. If we assume the same voltage in the newer cell structure, the power density would be increased from 9.4 to 16.1 watt-hours/pound.

In order to generally characterize the two-electrode system graphically as was done for the three-electrode system, it has been necessary to make the additional assumption that the voltage and power density at 40 ma/cm^2 would be at least as high as they were for the three-electrode system. In view of the fact that the voltage and power density are essentially the same at 1.5 ma/cm^2 and slightly higher at 17.0 ma/cm^2, it is felt that the assumption is conservative. This generalization is shown in Figure 19.

Extrapolation of power density with increasing anode capacity on the same basis as that used for the three-electrode system have been made. A summary of the results of the calculations are given in Table IX. A series of curves of power density versus current density are plotted in Figure 20. A comparison of the plots in Figure 11 to those in Figure 20 show that at low capacity the two-electrode system has considerably higher power density capability but as the two systems approach maximum capacity there is very little difference in terms of power density. Also because of the heavy cathode and because there is no saving in electrolyte weight by using two cathodes and two anodes, the double cell system is not effective as it is with the three-electrode system.

Cycle life for the two-electrode system has been generally shorter than for the three-electrode system under normal test conditions. Normal test conditions have consisted of charging for a fixed time, or to a voltage cut-off whichever came first, then discharging for a fixed time or to a low limit voltage cut-off. It was normal practice to set the current on charge

FIGURE 16.

REPRESENTATIVE CYCLE OF A TWO-ELECTRODE UNIT CELL (NO. 71) ON THE 2-HR. CHARGE/22-HOUR DISCHARGE REGIME AT 25° C

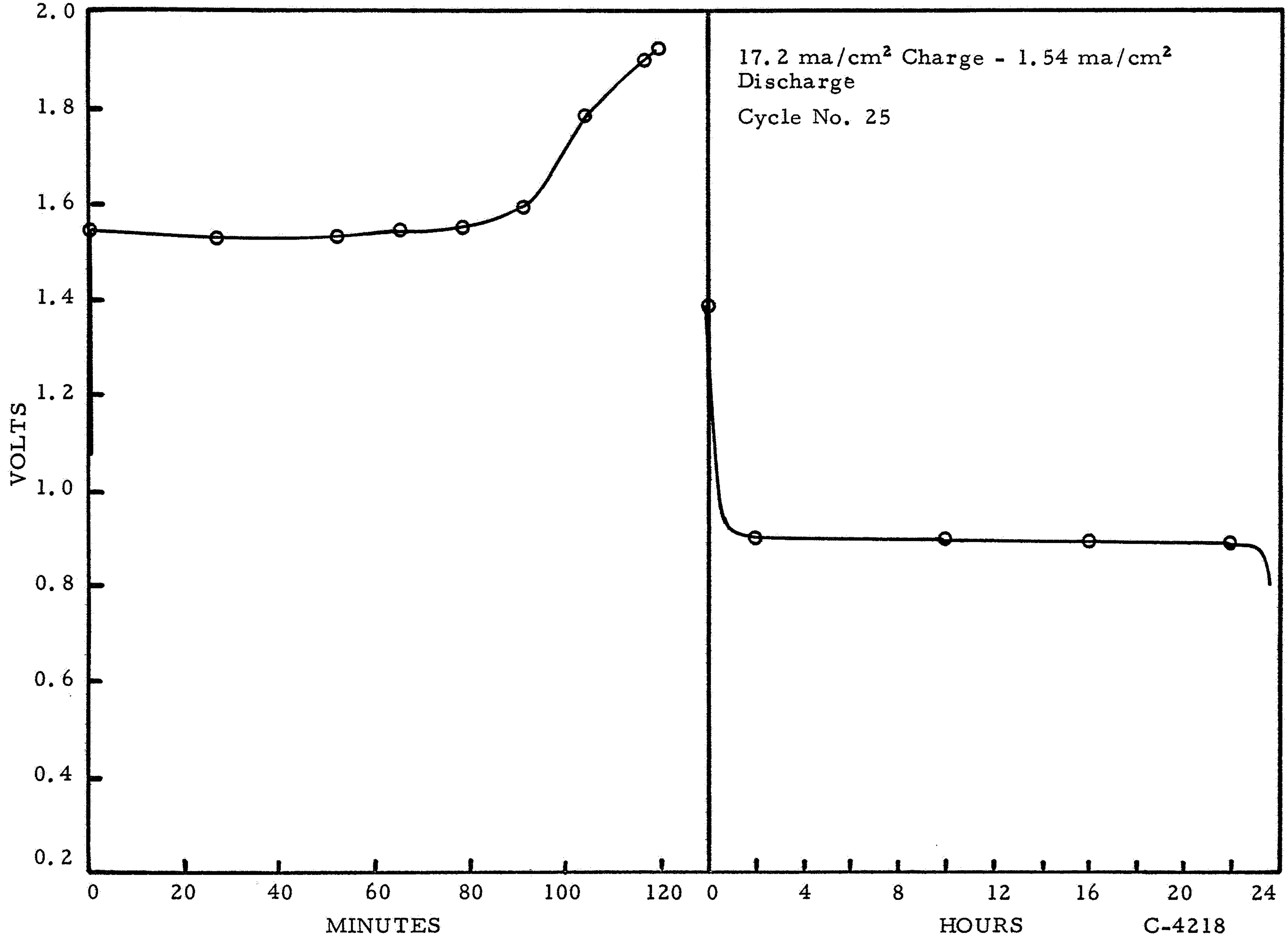


FIGURE 17.

REPRESENTATIVE CYCLE OF A TWO-ELECTRODE CELL (NO. 67) ON 22-HOUR CHARGE/ 2-HOUR DISCHARGE REGIME AT 25° C

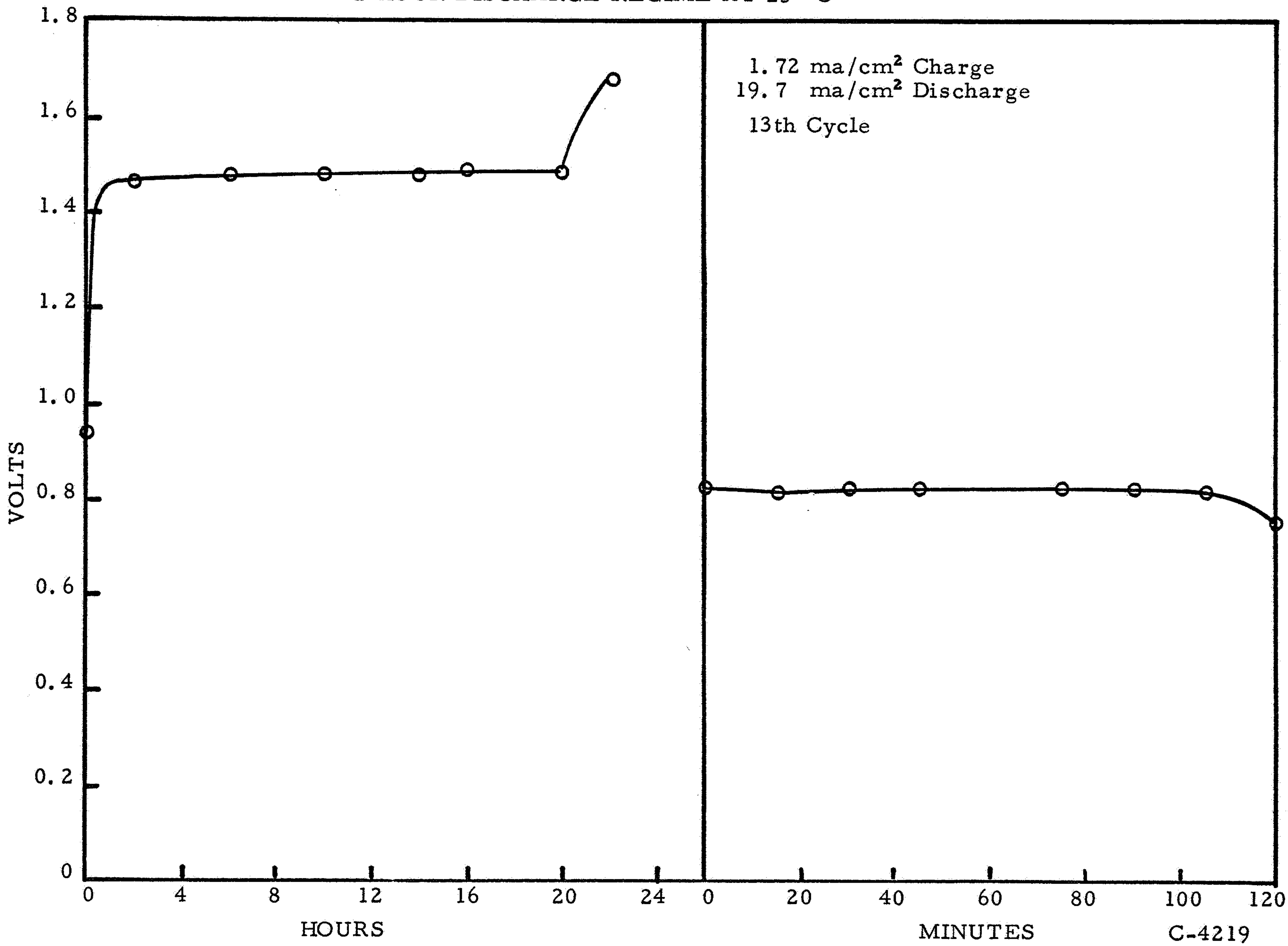
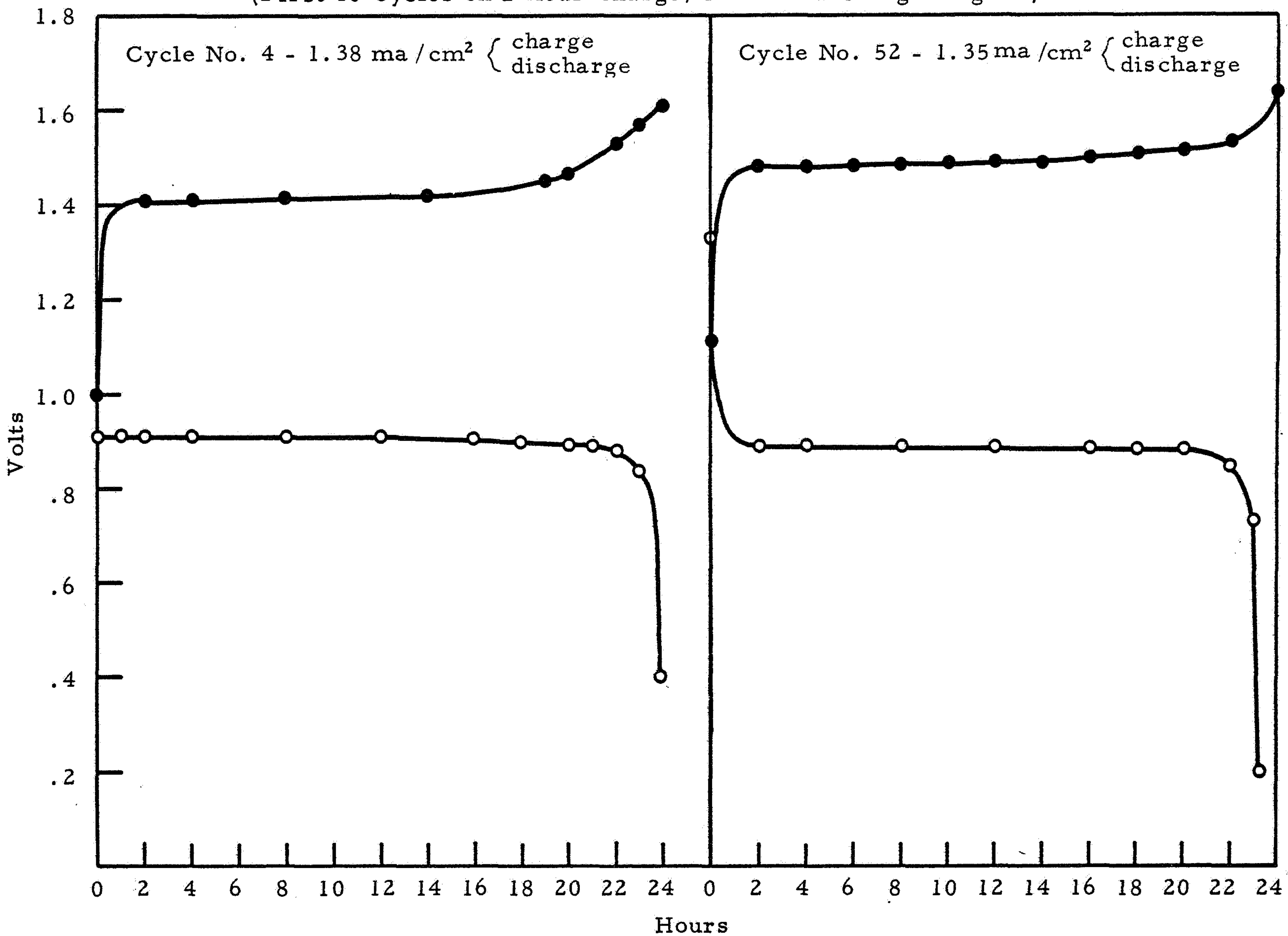


FIGURE 18

CHARGE AND DISCHARGE CURVES FOR THE TWO-ELECTRODE SYSTEM
AT THE 24-HOUR RATE AT 25°C
(First 40 Cycles on 2-Hour Charge / 2-Hour Discharge Regime)



C-3947

FIGURE 19.

ROOM TEMPERATURE CELL CHARACTERISTICS FOR THE TWO-ELECTRODE SYSTEM AFTER 100 HOURS OF OPERATION, BASED ON MOST RECENT CELL STRUCTURE

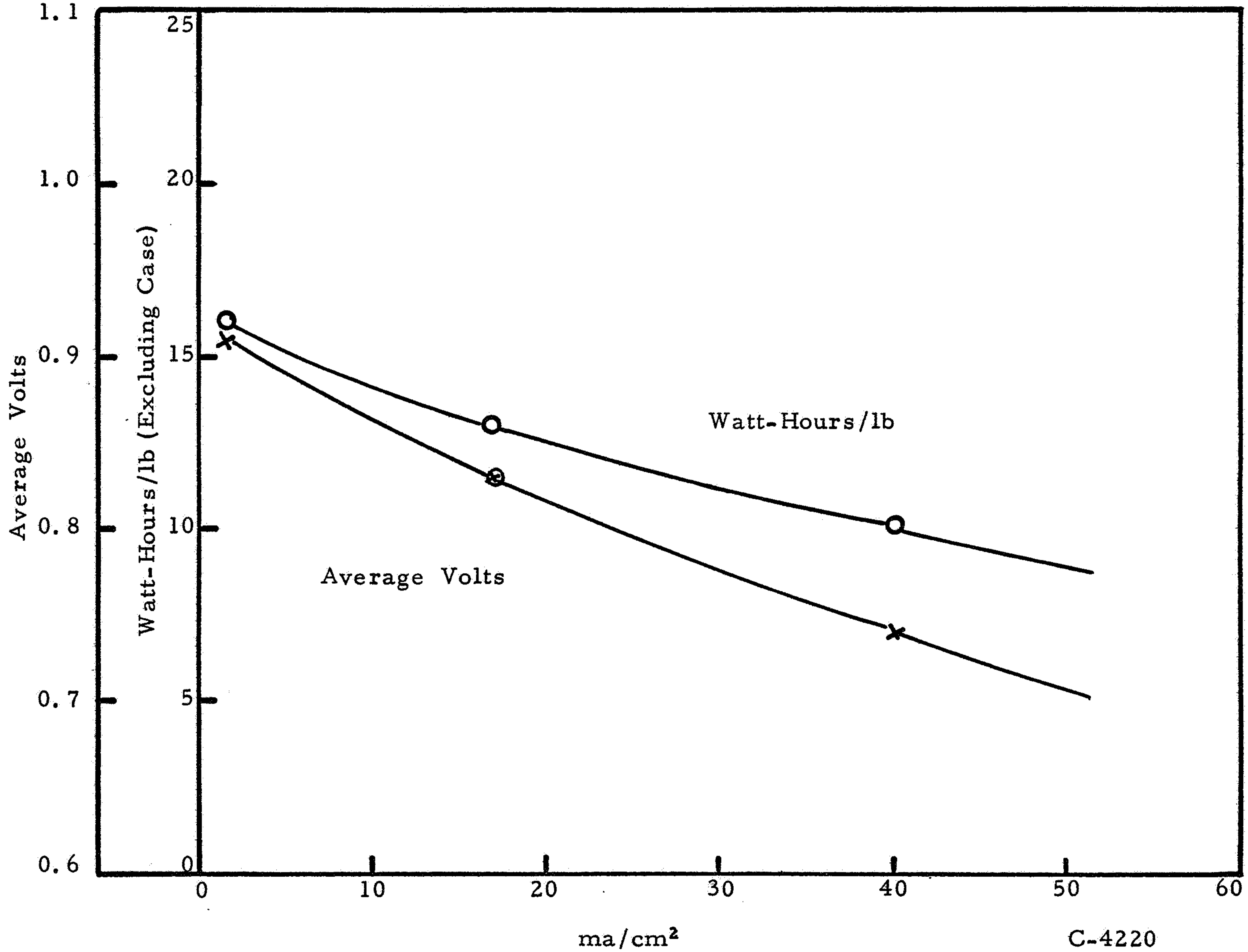


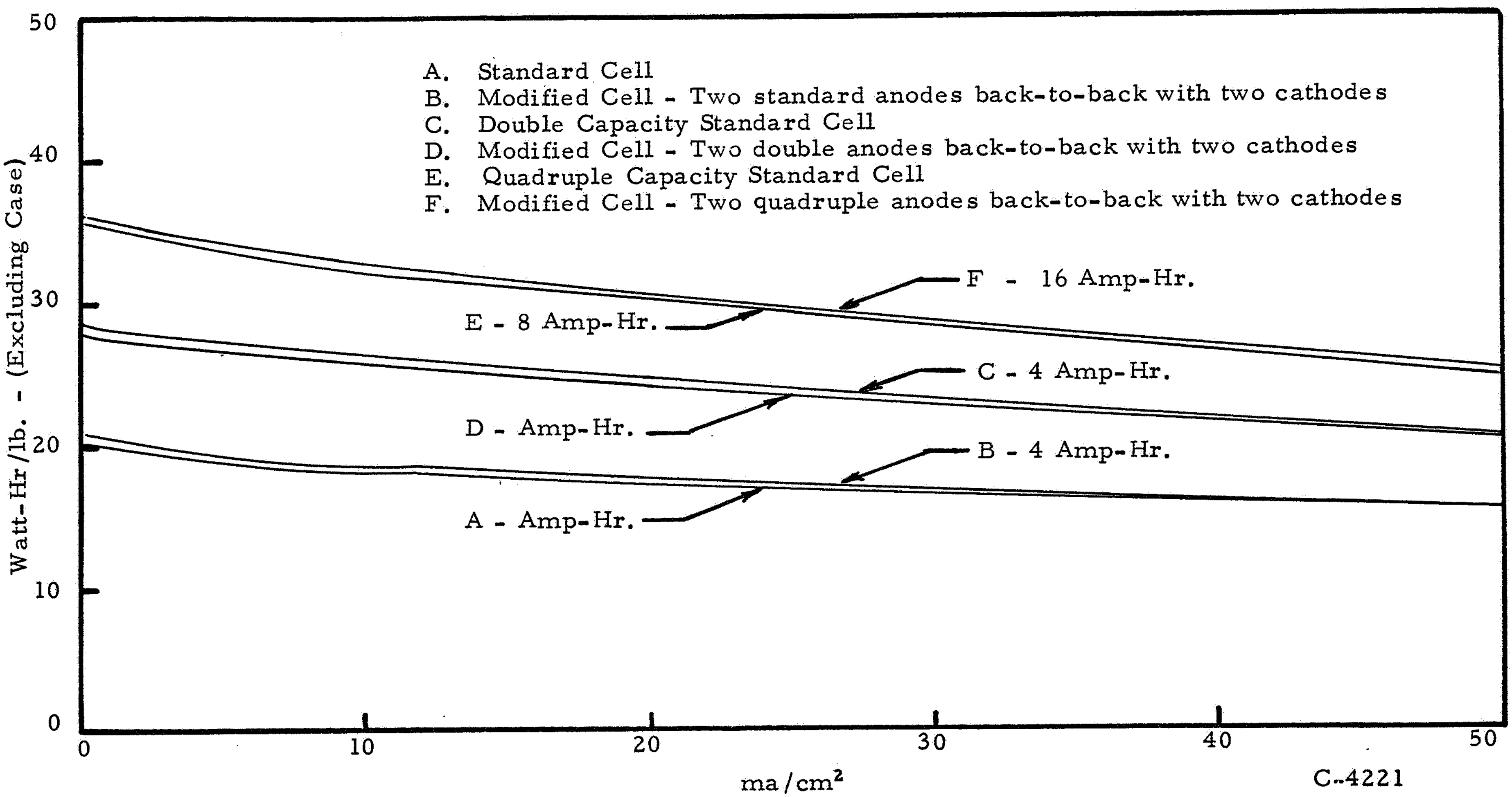
TABLE IX.

EXTRAPOLATION OF POWER DENSITY FOR HIGHER CAPACITY CELLS
FOR THE TWO-ELECTRODE SYSTEM (3" x 3" Cell Excluding Case)

	Component Weights for Extrapolation					
Components	Figure 4. Standard Cell (grams)	Double Capacity Anode (grams)	Two Single Anodes & Two Cathodes (grams)	Quadruple Capacity Anode (grams)	Two Double Anodes & Two Cathodes (grams)	Two Quadruple Anodes and Two cathodes (grams)
Anode and Lead	15.70	30.70	30.70	60.70	60.70	120.70
Cathode and Lead	15.84	15.84	31.68	15.84	31.68	31.68
Separator	1.20	1.20	2.40	1.20	2.40	2.40
Cathode Support (Gas space)	1.50	1.50	3.00	1.50	3.00	3.00
Electrolyte	8.00	9.86	16.00	13.58	21.99	25.71
Total Wt. (grams)	42.24	59.10	83.78	92.82	119.77	183.49
Total Wt. (lbs.)	0.093	0.130	0.184	0.204	0.264	0.404
Capacity (Amp-Hr)	2.0	4.0	4.0	8.0	8.0	16.0
Expected Av. Voltage at						
1.5 ma/cm^2	0.92 v	0.91 v	0.92 v	0.90 v	0.91 v	0.90 v
17.0 ma/cm^2	0.83 v	0.81 v	0.83 v	0.79 v	0.81 v	0.79 v
40.0 ma/cm^2	0.74 v	0.71 v	0.74 v	0.68 v	0.71 v	0.68 v
Watt-Hr/lb at						
1.5 ma/cm^2	19.8	28.0	20.0	35.3	27.6	35.6
17.0 ma/cm^2	17.8	24.9	18.0	31.0	24.6	31.3
40.0 ma/cm^2	15.9	21.8	16.1	26.6	21.5	26.9

FIGURE 20.

EXTRAPOLATION OF POWER DENSITY FOR HIGHER CAPACITY CELLS
TWO-ELECTRODE SYSTEM - 3 in. x 3 in. CELLS



and discharge so that the cell reached the voltage limit before the set time. The discharge voltage limit was always set at 0.4 volt or lower so that a full discharge would be attained. The charge voltage limit was set at 1.65 volts which is 0.15 volt above normal charging voltage and should ensure complete charging of the anode, and at the same time should limit the amount of hydrogen generated at the anode. (In the three-electrode system the charging voltage limit was set at 1.35 volts since the cathode is idle during charge.)

Under these test conditions, the LAB-40 cathode limited the charge rather than the anode. It was found that the cathode tends to have higher charging potentials with successive cycles, so that after a few cycles the cell reaches the charging cutoff voltage long before the anode has reached full charge. Successively higher cutoff voltages permit increased charge acceptance for a time until the continually rising potential of the cathode again limits the charge. This is illustrated by the behavior of Cell No. 20 in Figure 21. It has been established by reference electrode measurements that the change in potential on charging is almost entirely due to changes in the potential required to evolve oxygen from the cathode. The lower potential during discharge with repeated cycling is due in great part to more severe polarization of the cathode. The severity of this polarization is shown in Figure 22. This problem is shown even more dramatically in Figures 23 and 24 depicting the first and fourteenth cycles of Cell No. 17 where the charge cutoff voltage was set at 1.65 volts.

Attempts have been made to determine the cause of this cathode characteristic. Cells which were assembled with a third (charging) electrode still exhibited cathode polarization of the type shown in Figure 22. Regular two-electrode cells have been tested with extra precautions taken to exclude carbon dioxide. There was no benefit from rigorous exclusion of carbon dioxide as is shown in Figure 25. where the abnormally high charging potentials and lowered discharge potentials developed within seventy cycles. Chemical analyses of cell components have shown platinum in the electrolyte and on the anode, as well as traces of cadmium in the electrolyte and on the cathode. Loss of platinum, however, does not explain the cathode behavior

FIGURE 21.

CHARGE AND DISCHARGE CHARACTERISTICS OF CELL NO. 20
SHOWING SUCCESSIVELY HIGHER CHARGING POTENTIALS

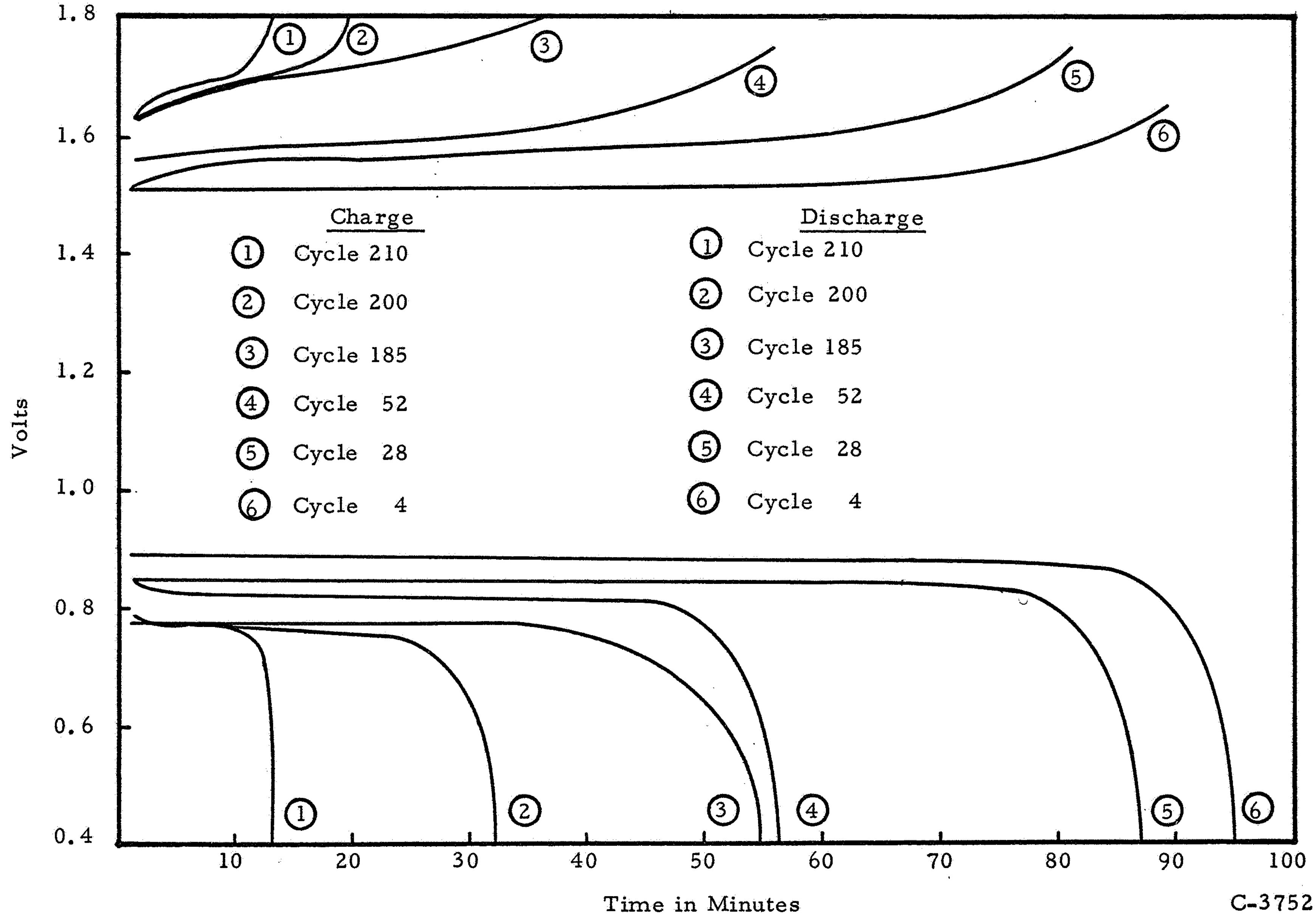


FIGURE 22.

IR FREE POLARIZATION OF OXYGEN ELECTRODE IN CELL NO. 20

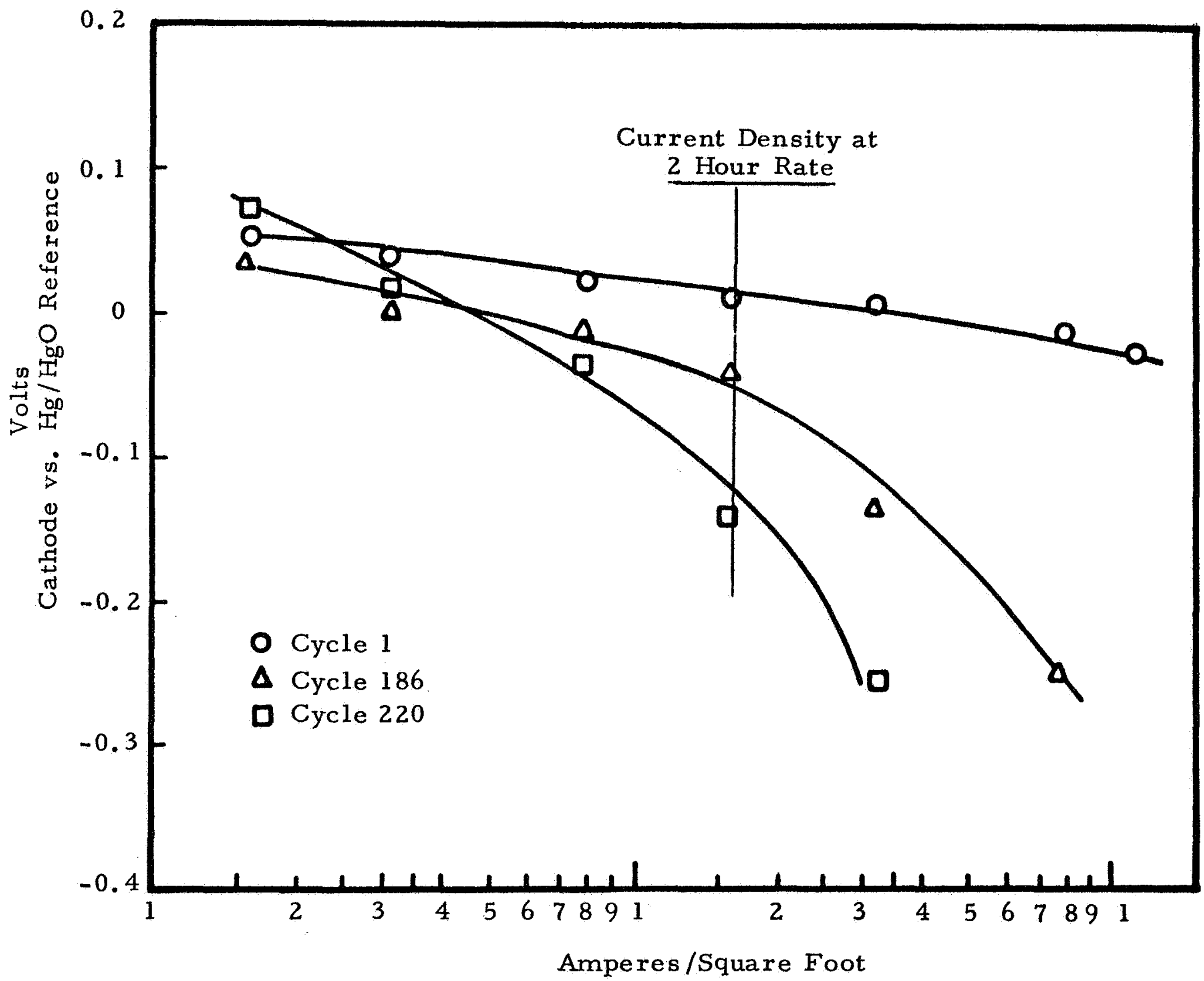


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FIGURE 23.

CELL NO. 17 - FIRST CYCLE AT 25° C AND 13.8 ma/cm²

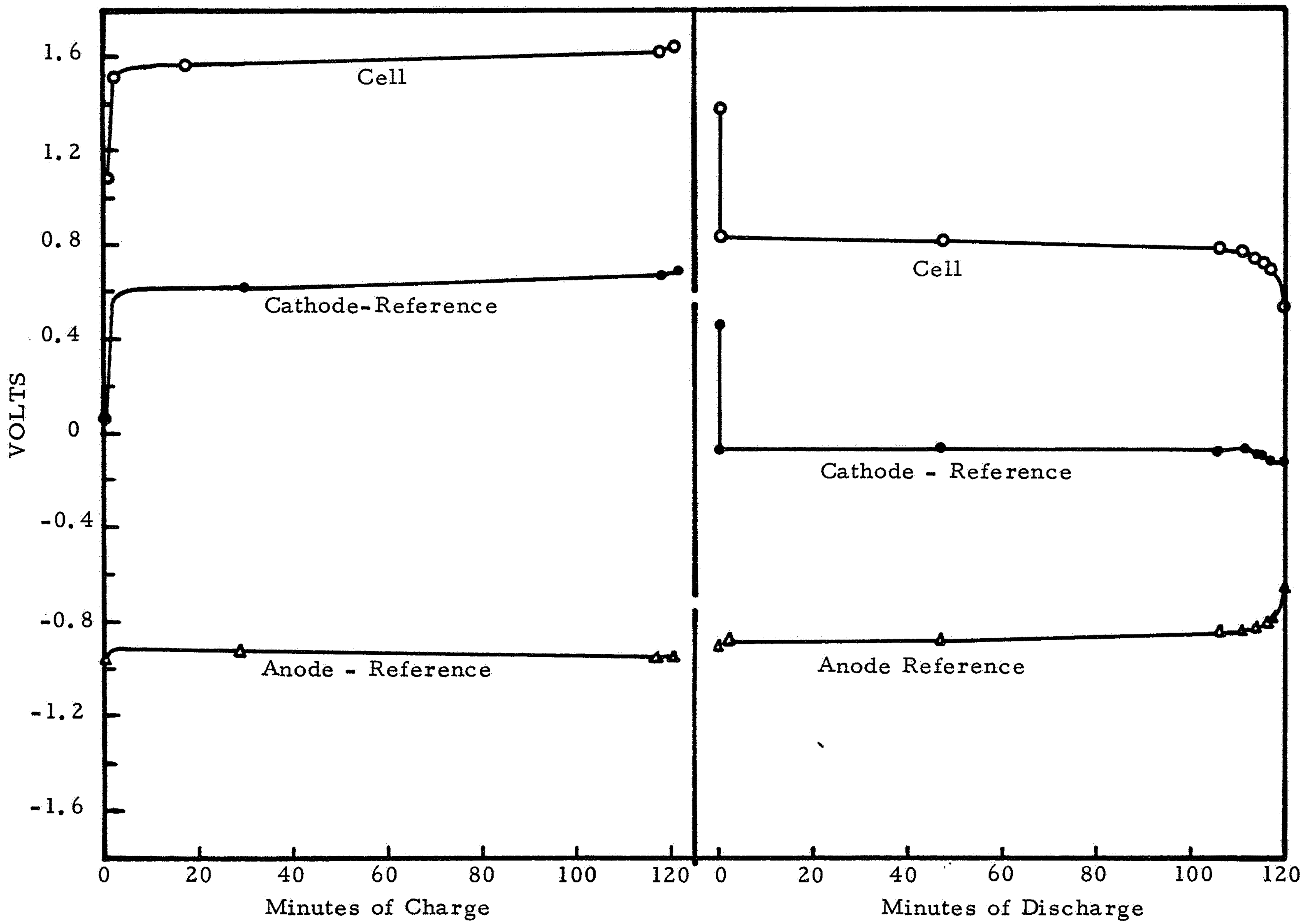

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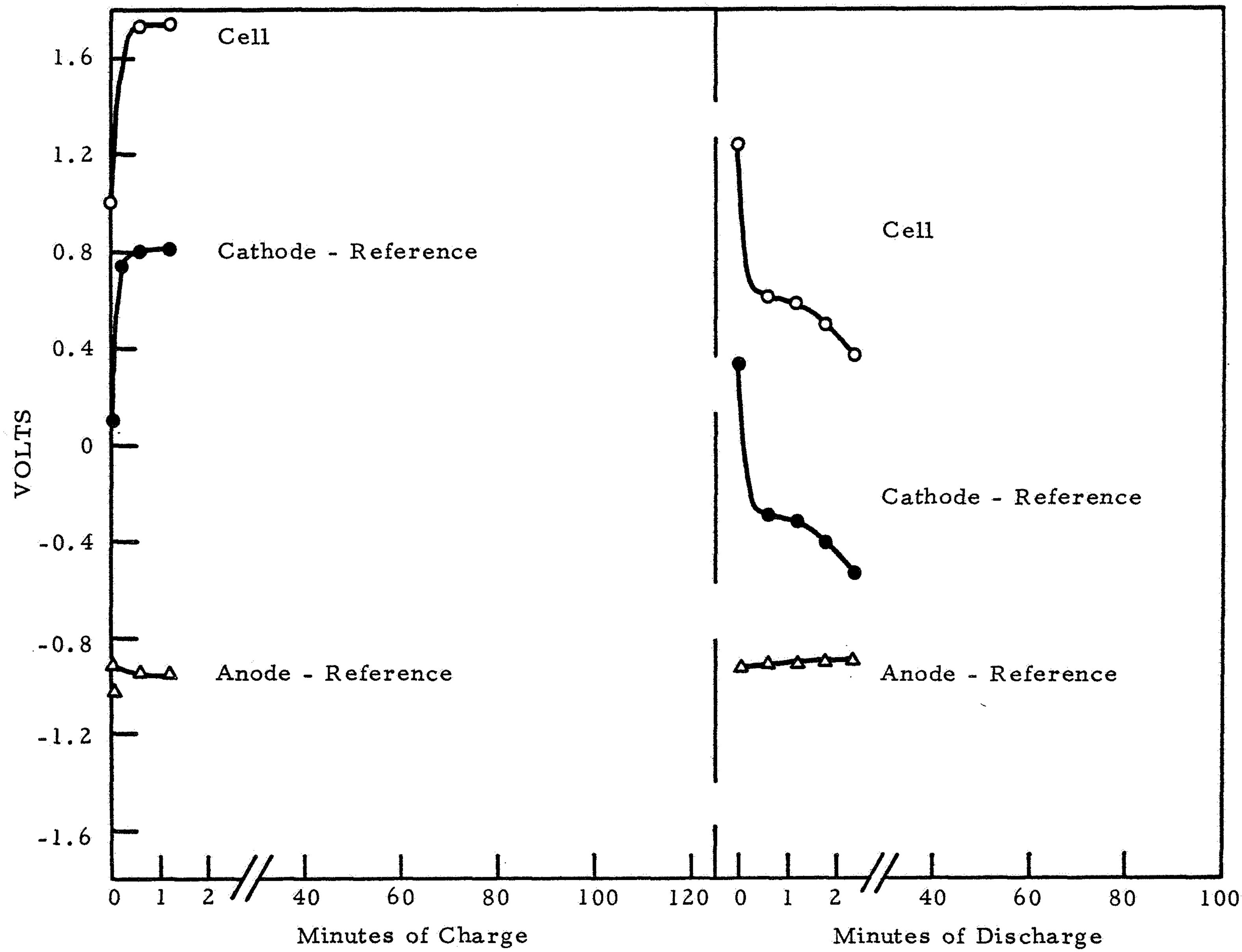
FIGURE 24.

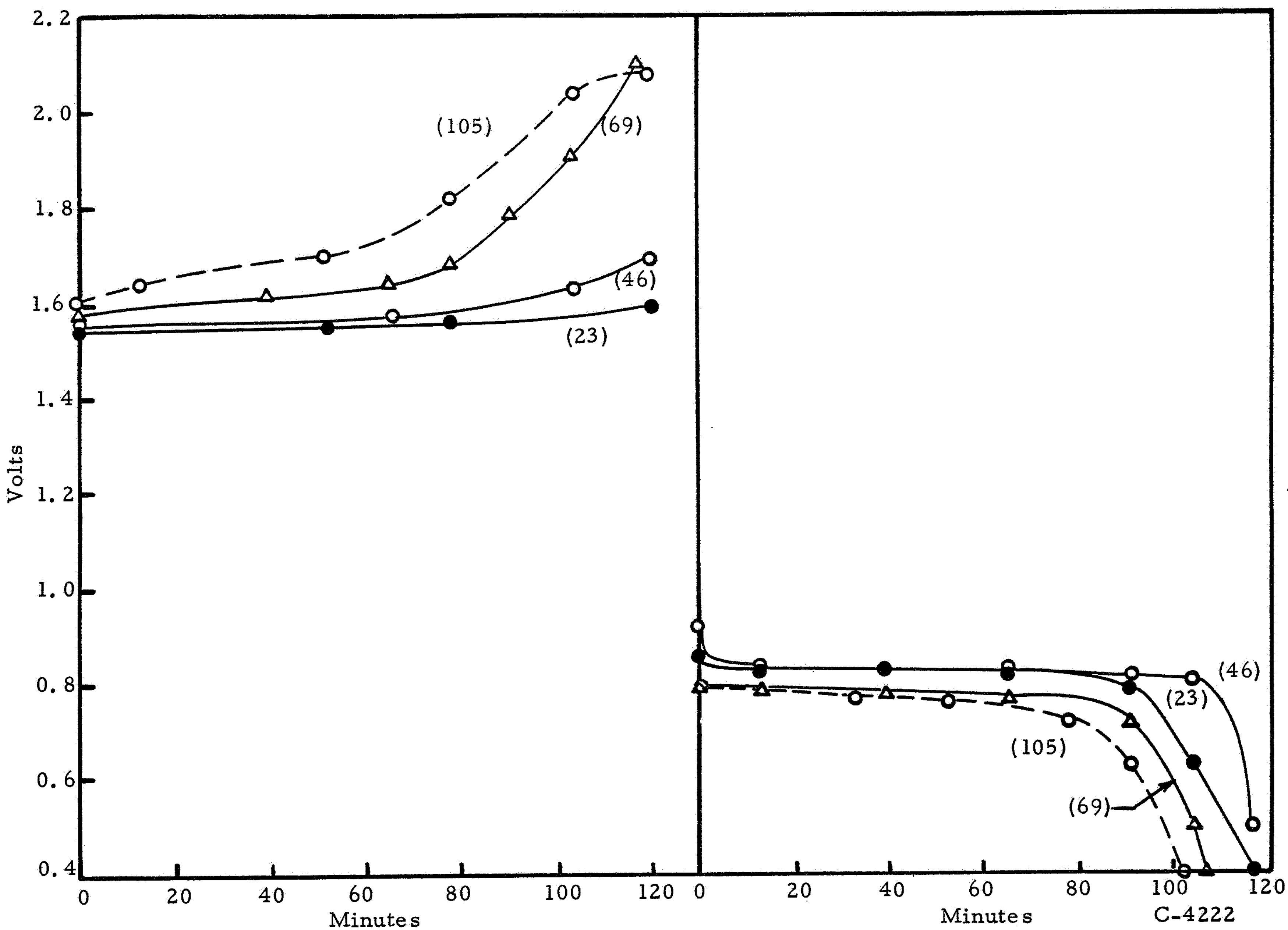
CELL NO. 17 - FOURTEENTH CYCLE
at 25° C and 13.8 ma/cm²



C-3941

FIGURE 25.

BEHAVIOR OF TWO-ELECTRODE CELL ISOLATED FROM ATMOSPHERIC CO_2
25° C - 17.2 ma/cm²



since degraded cathodes can be washed thoroughly, dried, and installed in a new cell where they give "like new" performance.

Two-electrode cell performance has been extended to over 800 cycles by the simple expedient of removing the voltage cutoff from the charge half of the cycle. Under these conditions, the charging voltage often exceeds 2.0 volts and there is a gradual degradation of discharge voltage. Cell No. 41 was placed on test and charged at constant current for two hours without a voltage cutoff. The cell was discharged at constant current to 0.4 volt. A few representative cycles throughout the life of the cell are shown in Figure 26. During the 260th cycle, reference electrode measurements were taken throughout the charge and discharge cycle resulting in the curves shown in Figure 27. A comparison of the time of discharge in the first cycle of Figure 26 with the anode versus Hg/HgO reference plot in Figure 27, shows that the anode capacity has decreased only about 4.5 per cent in 260 cycles. On the other hand, the cathode is polarizing severely after only 30 cycles. Further degeneration of the cathode is slower after the first thirty cycles.

There has been no definitely proven cause for this degradation of the American Cyanamid electrode, but it seems probable that it is related to the location of the liquid-gas interface within the electrode. It is believed that the behavior observed would occur if the liquid-gas interface should move inward (toward the gas face) until the interface was on the gas side of the screen current collector in the approximate center of the electrode. It is also believed that, at this stage, most of the gas generated on charging is evolved from the screen. Under these conditions gas generated could not escape from the gas side of the electrode as it does with a fresh electrode but would form gas pockets gradually pushing electrolyte out of the electrode preferentially toward the liquid face. This in turn would reduce the area of the electrode available to charging current with a resultant rise in charging voltage. On discharge, the gas pockets would provide a limited supply of oxygen highly available for initial fairly good discharge voltage. The electrode would then polarize as this supply was used up and the pores of the electrode filled with liquid.

In an attempt to confirm the gas-liquid interface location as the cause of cathode degradation, we made up two cells with asbestos separators and only

FIGURE 26.

CHARACTERISTICS OF CELL NO. 41 CHARGED WITHOUT VOLTAGE CUTOFF
25° C - 15 ma/cm² Charge and Discharge

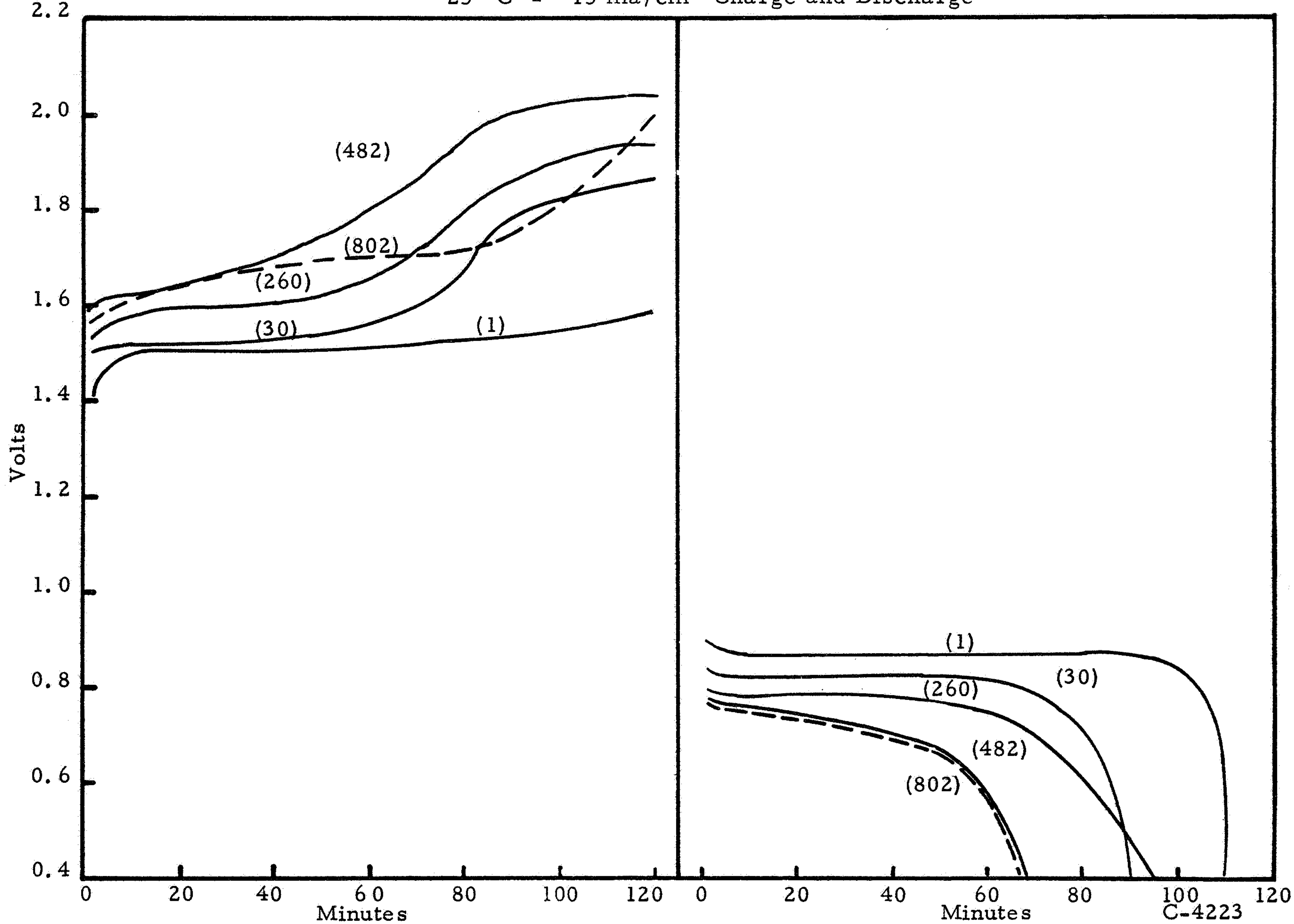
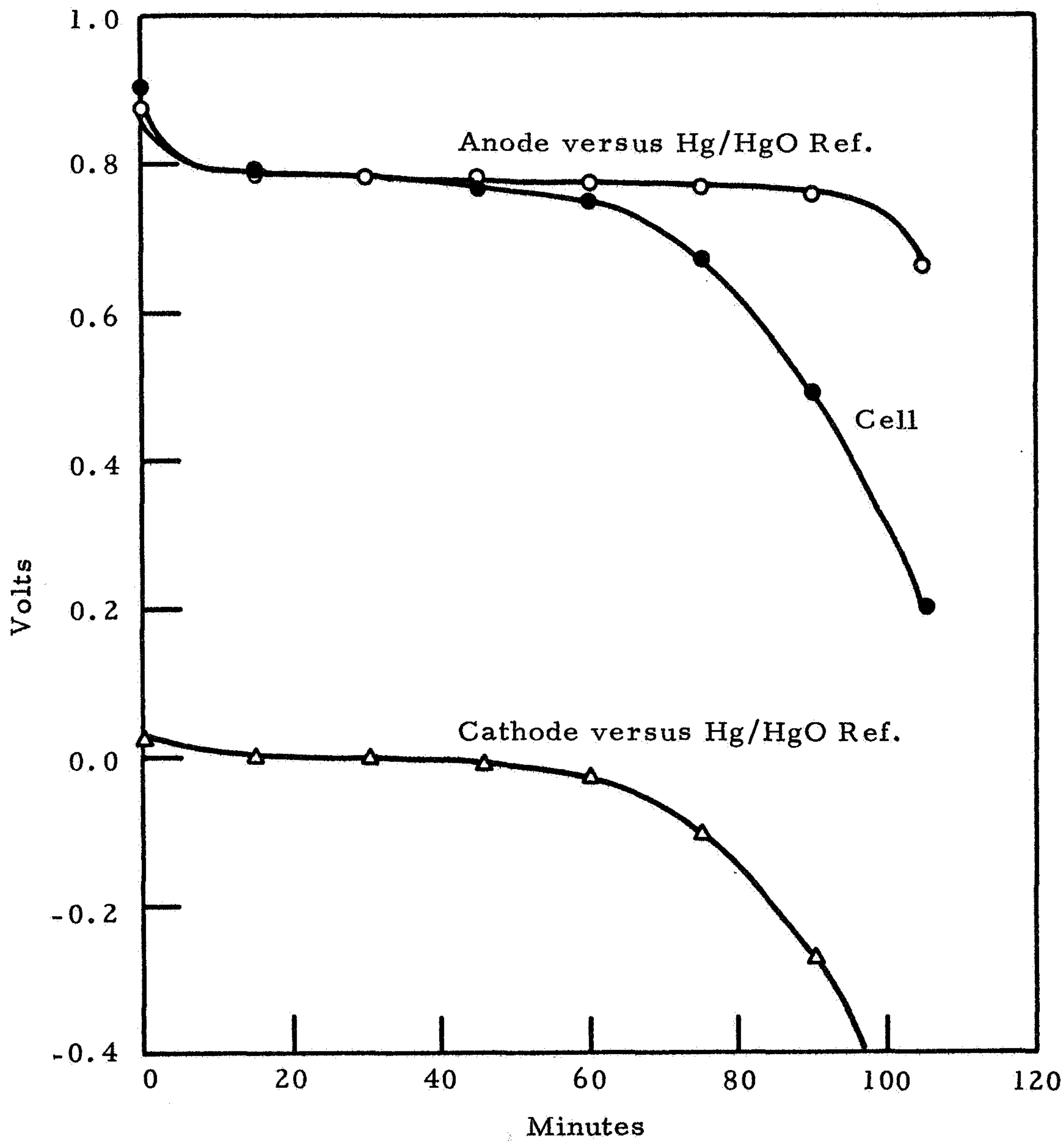


FIGURE 27.

ELECTRODE PERFORMANCE FOR CELL No. 41
ON THE 260th CYCLE SHOWING
CATHODE POLARIZATION AT 15 ma/cm²



C-3945

the quantity of electrolyte which could be wicked up by the separator and anode. These cells showed a rapid loss of capacity, but it was later discovered that the choice of separator material was an unfortunate one. Subsequent tests have shown that whenever asbestos is used the cadmium anode loses capacity quite rapidly as shown in Figure 28. This particular cell was operating as a wick-type cell with asbestos separators at a current density of 9 ma/cm^2. Reference electrode measurements showed the anode had lost capacity, but that the cathode was functioning normally. On the other hand polarization measurements of the cathode of another cell (Wick-Type No. 1) shows an improvement in the cathode after 50 cycles as shown in Figure 29. The postulated cause of LAB-40 electrode degeneration is at least partially substantiated by the cathode stability shown here.

At 40° C and at 0° C, test results have been obtained on the two-hour charge/two-hour discharge regime only. At 40° C the results have been very similar to those obtained with the three-electrode cells. More rapid wetting of the cathode with resulting shortened cycle life has been the major cause of failure. Cycle life has ranged from 90 to 275 cycles which is in the same range as that obtained with the three-electrode system. Typical charge and discharge curves are shown in Figure 30. for two different cells at 40° C.

Again at 0° C, the two-cell structures have quite common characteristics. Both are cathode-limited and cycle life is greatly reduced. After failure at 0° C, additional cycles can be obtained at room temperature. Cycle life is limited to about 10 to 40 cycles. Figure 31 shows typical charge and discharge curves for two cell at 0° C.

A few cells were made with LAB-6 cathodes with Type C backing and tested on the two-hour charge/two-hour discharge regime at 25° C. These cathodes have characteristics very similar to the LAB-40 type during the charge half of the cycle. On discharge, however, they have a much lower operating voltage and have a tendency to develop a voltage dip during the first few minutes of discharge. The 59th cycle of Cell No. 73, is plotted in Figure 32 and shows these characteristics of the LAB-6 electrode.

FIGURE 28.

EFFECT OF ASBESTOS SEPARATOR ON CAPACITY OF CADMIUM-OXYGEN CELLS (WICK TYPE) 25°C - 9 ma/cm^2

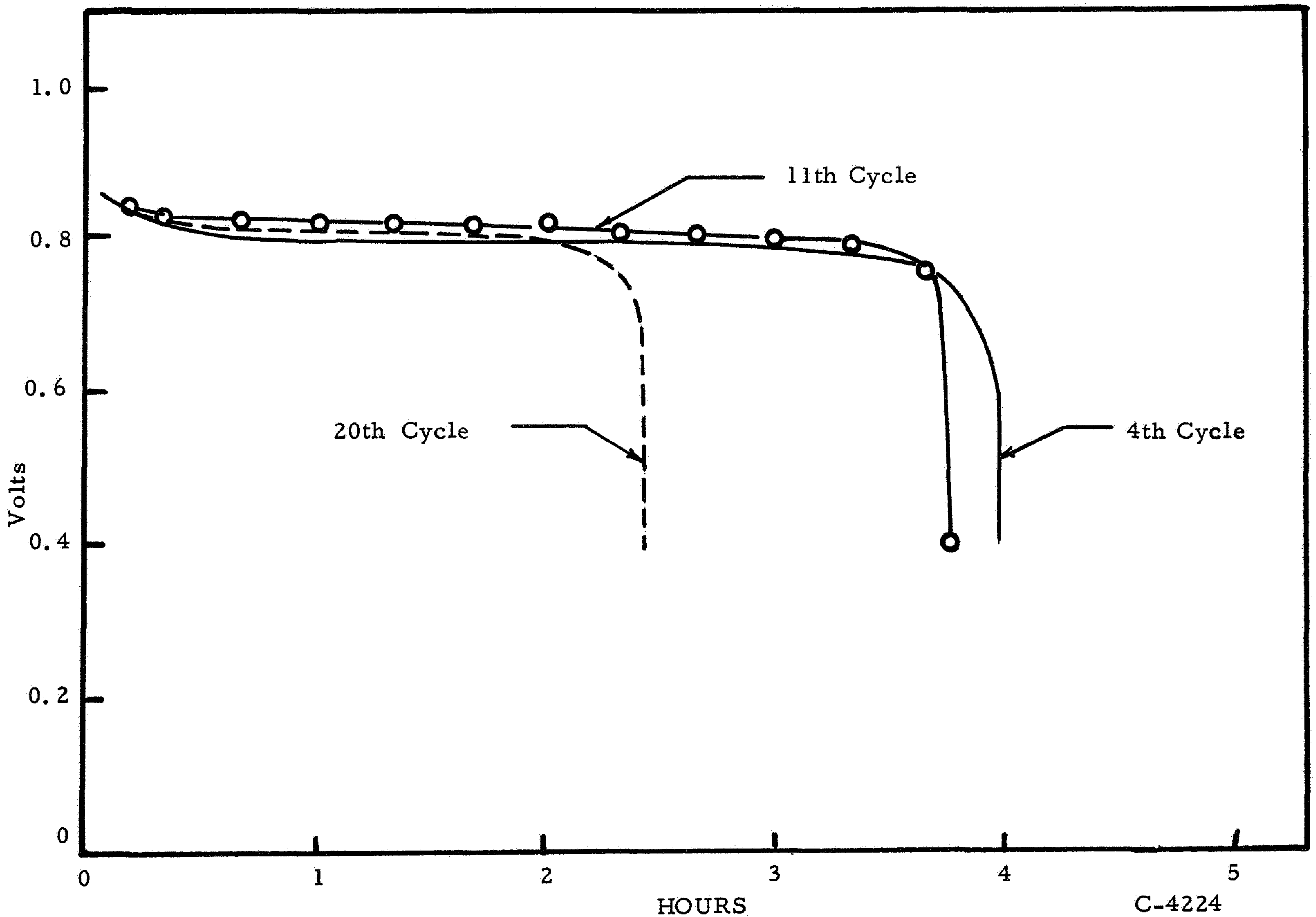


FIGURE 29.

IR FREE POLARIZATION CURVES FOR WICK TYPE CELL NO. 1 - CATHODE, LAB-40, AT 25° C

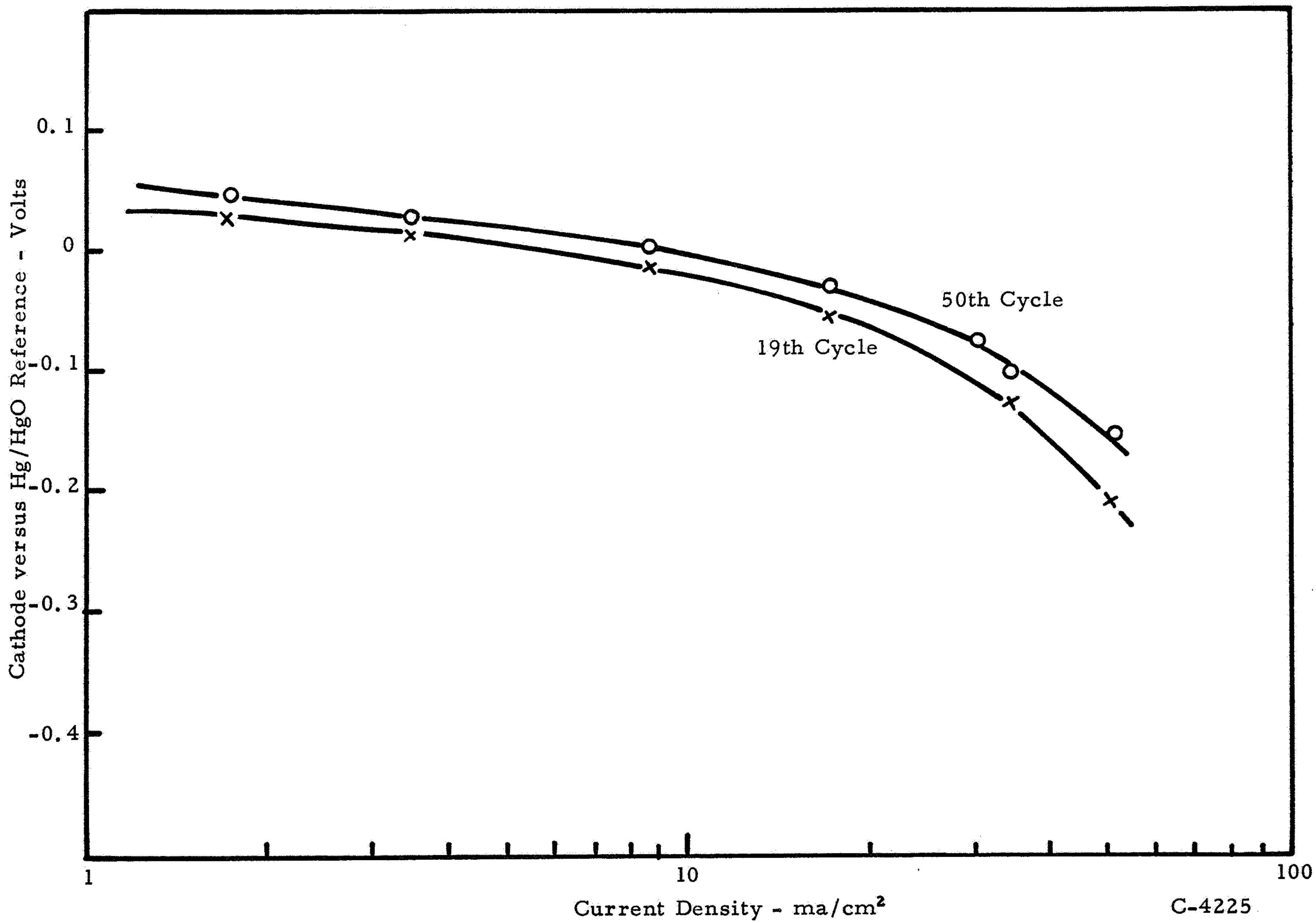


FIGURE 30.

TYPICAL CHARGE/DISCHARGE CURVES OF TWO-ELECTRODE UNIT CELLS AT 40° C

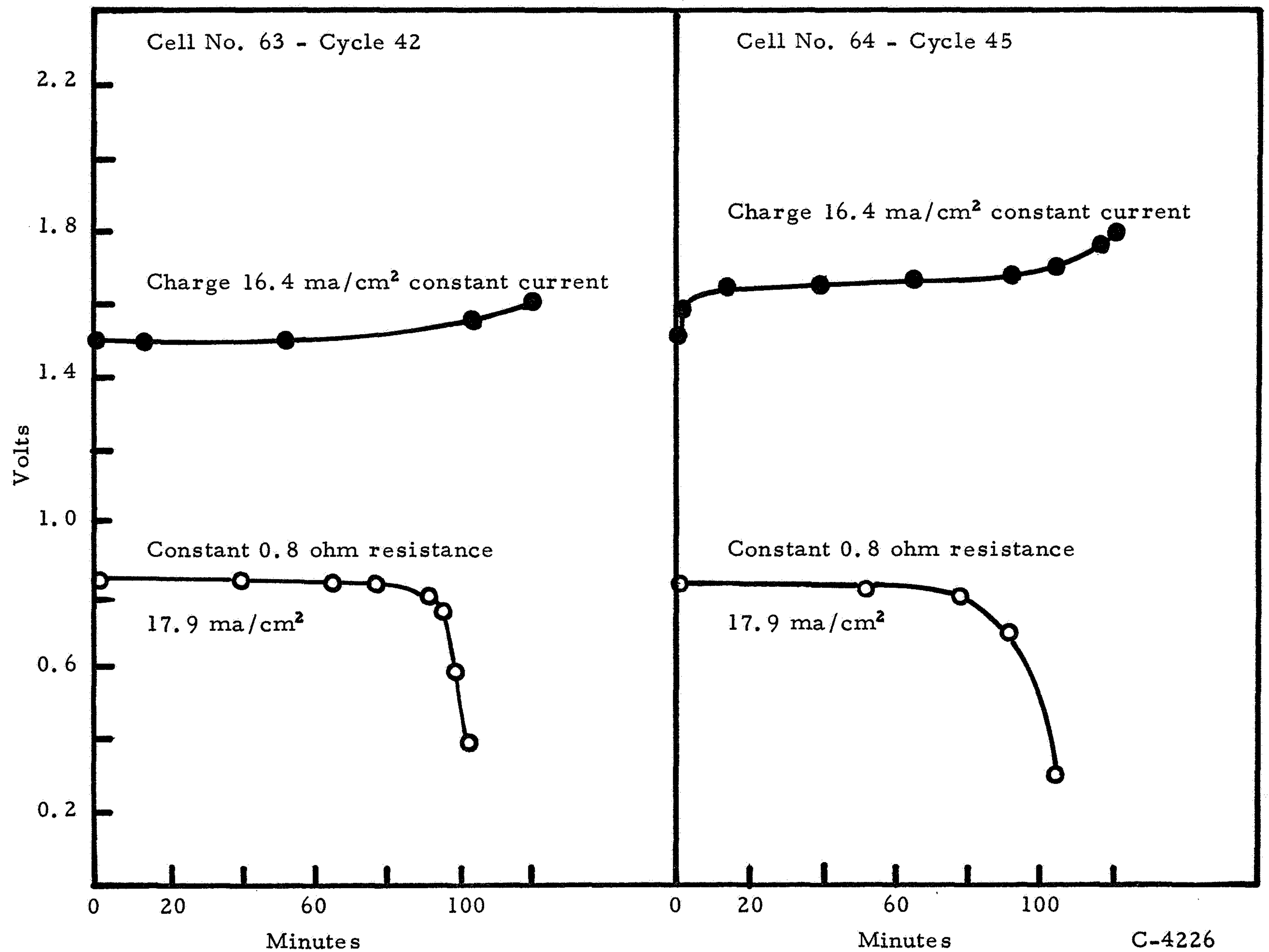


FIGURE 31.

TYPICAL CHARGE AND DISCHARGE CURVES FOR TWO-ELECTRODE CELL AT 0° C

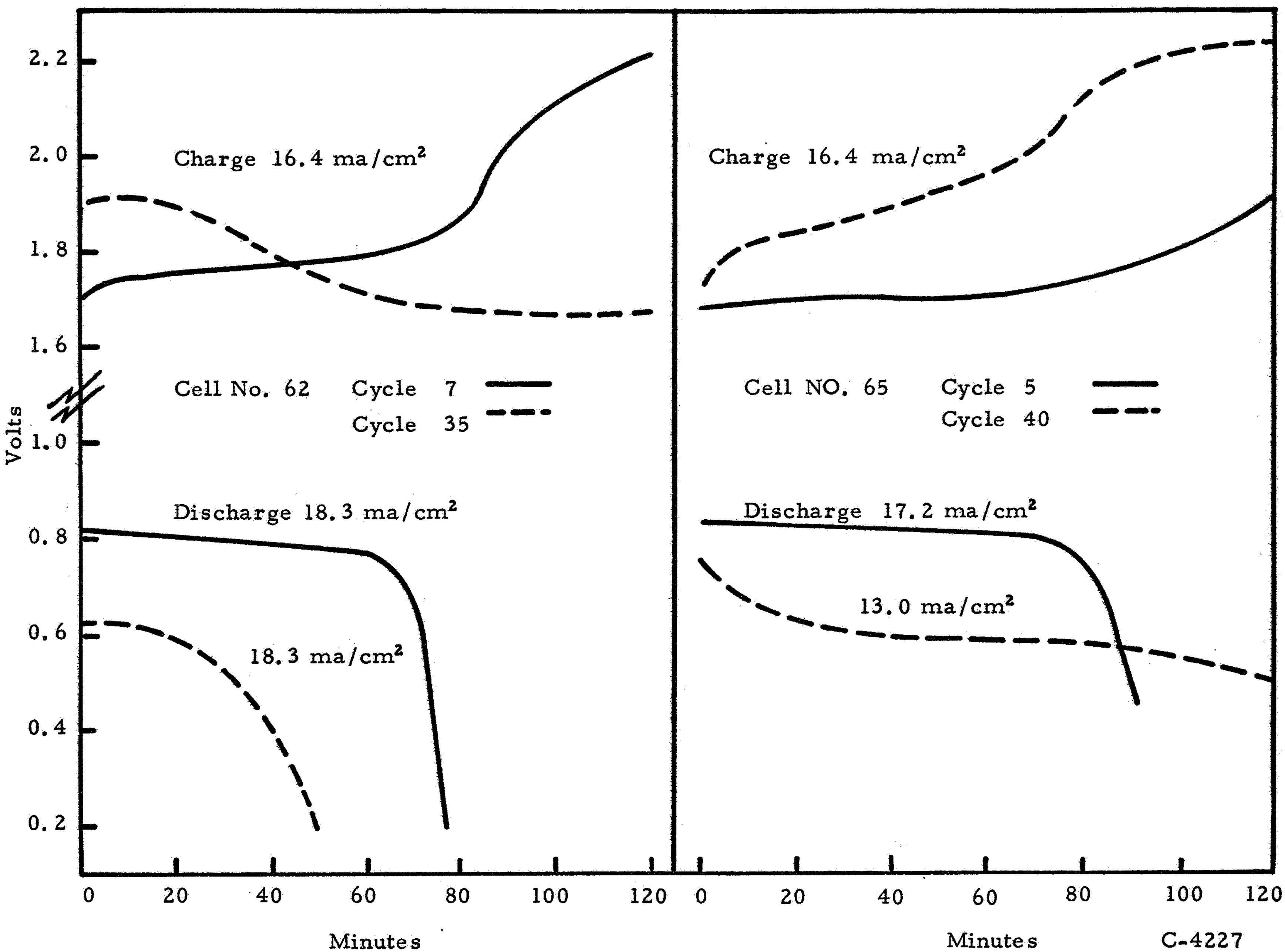


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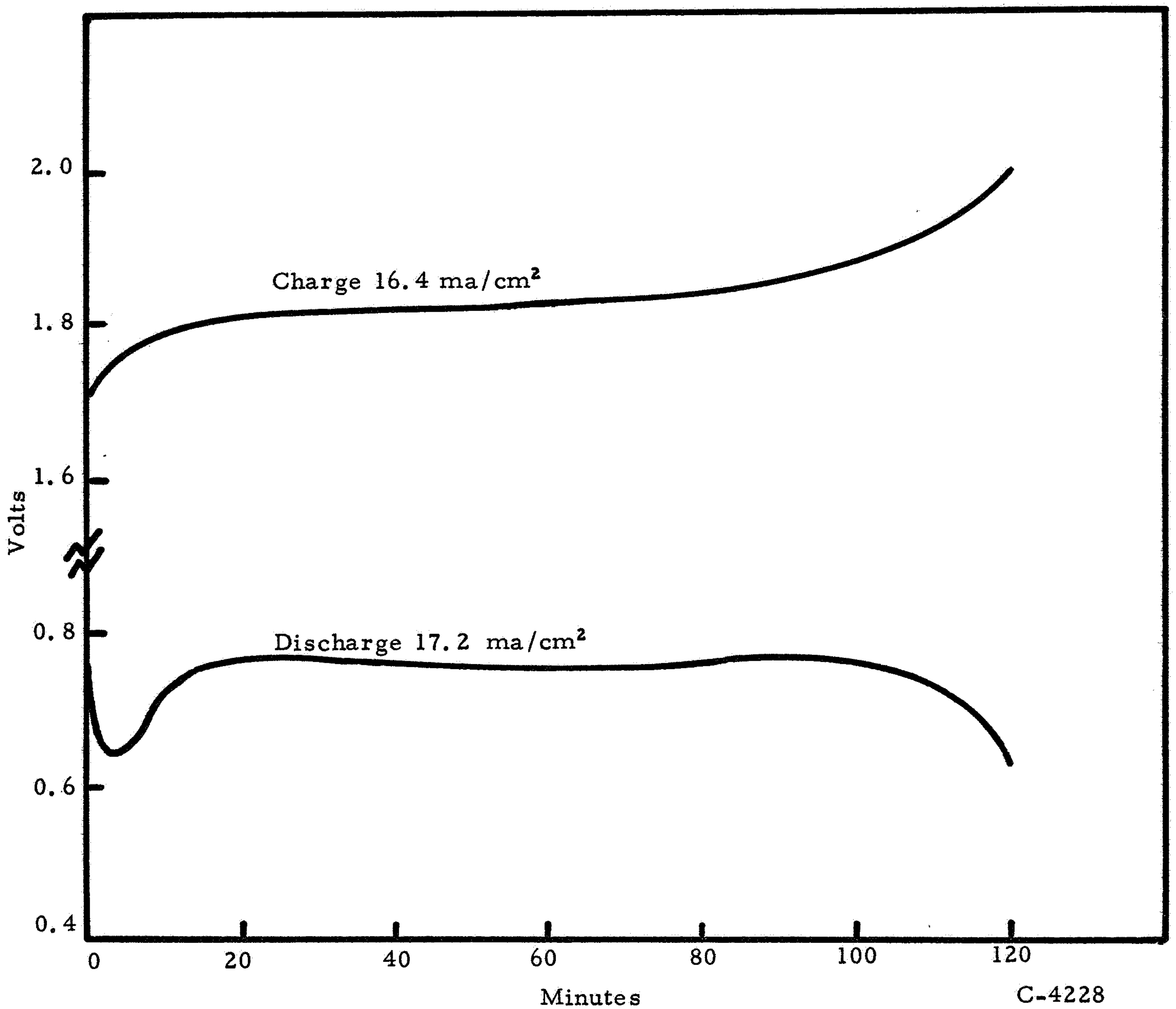
FIGURE 32.

CHARACTERISTICS OF A TWO-ELECTRODE CELL WITH A LAB-6 CATHODE AT 25° C
Cell No. 73 on 59th Cycle



3. Prototype Cells

As material representative of the contract effort sixteen single cells have been built and delivered to NASA. In order to provide examples of cells containing both American Cyanamid and Union Carbide cathodes in configurations discussed in the report, cells were supplied in three variations. The three groups of cells were provided as follows:

(a) Four cells were constructed with Union Carbide T-2 cathodes, Union Carbide electrodeposited cadmium anodes, and nickel mesh charging electrodes located between the anode and cathode.

(b) Four cells were constructed as above except that the nickel mesh charging electrode was located on the opposite side of the anode from the cathode.

(c) Eight cells were constructed with American Cyanamid Lab-40 cathodes with type B-II-4 backing, Union Carbide electrodeposited cadmium anodes, and a nickel mesh charging electrode located on the opposite side of the anode from the cathode. The addition of the charging electrode provides the option of operating these cells as either two or three-electrode systems at the discretion of NASA.

Included in this report as Appendix I is a "Table of Typical Component Weights" for cells containing the two types of cathodes, a "Table of Order of Assembly" for the three variations outlined above, and a "Procedure for Activation of Cadmium-Oxygen Cells".

4. Design Study

A study has been made to design a 28-volt, 3 KWH secondary battery based on the cadmium-oxygen system. Although the contract calls for the study to be based on a twenty-four-hour charge, this study has been expanded to include designs based on a two-hour charge/two-hour discharge and a twelve-hour charge/twelve-hour discharge. The additional studies permit plotting of curves for power density versus design discharge rate. The design study has been made on a conservative basis and shows watt-hr/lb capabilities of 15.65 at the two-hour rate, 18.97 at the twelve-hour rate and 19.55 at the twenty-four-hour rate including oxygen tankage and auxiliary equipment. The design study is included in this report as Appendix II.

NEW TECHNOLOGY

There have been no new technological advances falling within the scope of this contract.

CONCLUSIONS AND RECOMMENDATIONS

The cadmium-oxygen system has been found to be capable of about 500 charge and deep discharge cycles at 25° C with the cathodes now available. Cycle life has been cathode-limited for both Union Carbide T-2 electrodes and American Cyanamid LAB series electrodes. At room temperature the Union Carbide Corporation T-2 electrode provides slightly better cycle life, but cells must include a third electrode for charging. The American Cyanamid LAB-40 electrode can be used without an auxiliary charging electrode, but has a tendency to deteriorate more rapidly than the Union Carbide Corporation T-2. The American Cyanamid LAB-6 electrode operates at a much lower voltage and is not considered suitable for this service.

At 0° C neither of the two cathodes are capable of long cycle life, but both appear to be capable of operating for a few cycles at 0° C. After cathode failure at 0° C, they can be operated again if warmed to room temperature. At 40° C the cycle life is again lower than that normally found at 25° C, but much better than at 0° C. Evaporation of electrolyte and loss of electrolyte repellency of the cathodes are the main problems at the elevated temperature. Normal cycle life is 10 to 70 cycles at 0° C, and 100 to 250 cycles at 40° C.

On the basis of data obtained, power density calculations show that the two-electrode system is superior to the three-electrode system. However, with anodes of high capacity the extra weight of the LAB-40 cathode offsets the added weight of the charging electrode. On the other hand, the use of a third electrode requires additional circuitry to accommodate changing the current path between the cathode and the charging electrode. The complicated circuitry required for the three-electrode system is an important factor in recommending the two-electrode system for use in the design study (appended) of a 28 volt, 3 KWH battery.

The system has been operated inside a closed vessel so that the oxygen generated on charge has been consumed during discharge repeatedly. The danger of generating hydrogen and oxygen together has been minimized by using a platinum catalyzed "getter" for the hydrogen. With this arrangement considerable overcharge has been possible with no indication of hydrogen accumulation.

The charge acceptance of the anode is very good in the flooded cell structure (anode covered with liquid electrolyte). Less than 5 per cent overcharge is necessary to completely charge the anode. In the wick-type cell structure where an adequate separator has not yet been found, the apparent anode charge acceptance is not as good in that about 20 per cent overcharge is required.

In view of the experimental results showing rechargeability with reasonable cycle life, excellent charge acceptance and relatively high power density capabilities, it is recommended that the cadmium-oxygen system should be further evaluated in multiple cell batteries. At least part of the continued effort should be in completely enclosed systems where the oxygen generated on charge is reused on discharge. It is also recommended that as new or improved cathodes become available from any source, they should be evaluated in this system with respect to improved cycle life.

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APPENDIX I

DESCRIPTION AND SPECIFICATIONS OF PROTOTYPE CELLS

TABLE I.

TABLE OF TYPICAL COMPONENT WEIGHTS

	UCC T-2	Am. Cy. Lab-40
Cathode with Lead	12.15 g	15.84 g
Anode with Lead	15.70	15.70
Chg. Elect. Assembly	3.73	3.73
Pellon Separators	1.20	1.20
Cathode Support (Ni)	1.93	1.93
Framing & Epoxy	64.68	64.68
Avg. total cell weight	106.54 g	110.23 g

TABLE II.

TABLE OF ORDER OF ASSEMBLY
(From Left to Right)

Cell No.	Cathode Support	Cathode	Chg. Assembly Gas Escape Space	Chg. Assembly Charge Elect.	"A"* Separator	Cd Anode wt. gms.	"B"* Separator	Chg. Assembly Charge Elect.	Chg. Assembly Gas Escape Space	Total Cell
G2-1	Ni	T2	--	--	Pellon	15.44	Pellon	Ni	0.060"	106.95
G2-3	Ni	T2	--	--	Pellon	15.91	Pellon	Ni	0.060"	104.19
G2-4	Ni	T2	--	--	Pellon	15.83	Pellon	Ni	0.060"	105.93
G2-5	Ni	T2	--	--	Pellon	15.61	Pellon	Ni	0.060"	103.96
G2-7	Ni	T2	0.060"	Ni	Pellon	16.05	Pellon			107.73
G2-8	Ni	T2	0.060"	Ni	Pellon	16.15	Pellon			110.64
G2-9	Ni	T2	0.060"	Ni	Pellon	15.28	Pellon			105.66
G2-10	Ni	T2	0.060"	Ni	Pellon	15.43	Pellon			107.24
G2-11	Ni	Lab-40	--	--	Pellon	Cd	Pellon	Ni	0.060"	110.10
G2-12	Ni	Lab-40	--	--	Pellon	Cd	Pellon	Ni	0.060"	108.83
G2-13	Ni	Lab-40	--	--	Pellon	Cd	Pellon	Ni	0.060"	109.08
G2-14	Ni	Lab-40	--	--	Pellon	Cd	Pellon	Ni	0.060"	109.80
G2-15	Ni	Lab-40	--	--	Pellon	Cd	Pellon	Ni	0.060"	110.35
G2-16	Ni	Lab-40	--	--	Pellon	Cd	Pellon	Ni	0.060"	113.18
G2-17	Ni	Lab-40	--	--	Pellon	Cd	Pellon	Ni	0.060"	109.91
G2-18	Ni	Lab-40	--	--	Pellon	Cd	Pellon	Ni	0.060"	110.59

*Pellon - No. 2505W - 1.20 grams/cell

Charging Assembly - Expanded nickel grid plus 8 pieces .020 inch x .080 inch vinyl spacers fused 3.73 grams/cell

MEMORANDUM

To: W. G. Darland

From: V. R. Osmialowski

Subject: PROCEDURE FOR ACTIVATION OF CADMIUM-OXYGEN UNIT CELLS

1. Remove cell from individual container and start oxygen feed prior to filling. Recommended gas feed at 0.025 to 0.05 SCFH per ampere of load, and a pressure head of two to three inches of water at the outlet port. The gas feed may be humidified to minimize electrolyte evaporation.

2. Fill cell with 40 percent KOH; sp. gr. = 1.40 - 1.42 g/ml. Use standard reagent grade KOH and distilled water. Without removing the cover plate fill the cell through either port at the top to the liquid level mark. In case of evaporation from the cell, refill with distilled water during charging. Electrode gassing will then mix the solution.

3. All cells have been provided with charging electrodes. These must be used to charge the following cells:

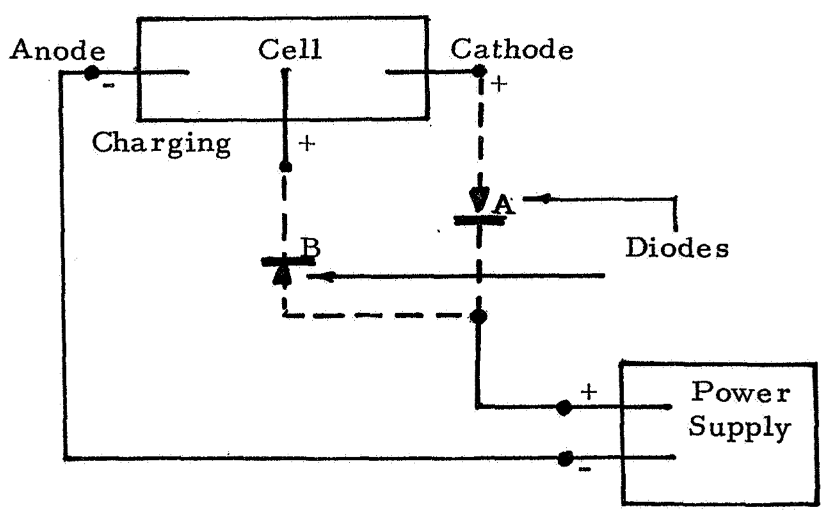
   G 2-1; G 2-3; G 2-4; G 2-5;
   G 2-7; G 2-8; G 2-9; G 2-10.

   Use of the charging electrode in other cells is optional and at the discretion of the testing engineer.

   The three-electrode unit cell can also be charged as a two-electrode cell with the proper connection of two diodes into the charging circuit. Two diodes must be used to prevent charging of both charging electrode and cathode in parallel. Figure 1 is a schematic drawing showing the positioning of the diodes.

FIGURE 1

CHARGING CIRCUIT FOR THREE-ELECTRODE UNIT CELL USING DIODES



When positioned properly, charging will be accomplished by the use of the anode and charging electrode with diode A blocking current flow to the oxygen electrode. During discharge, diode B blocks current flow through the charging electrode.

To charge, connect the positive lead of the power source to the charging electrode lead and the negative lead to the negative lead of the battery. To discharge at constant current, the positive lead of a constant current source is connected to the negative terminal of the cell and the negative lead of the source to the positive terminal of the cell. For a fixed resistance discharge, connect the proper resistor across the positive and negative terminals of the cell. Cell voltage is measured across the anode (negative) and the cathode (positive) terminals at all times.

4. Recommended high rate of charge and discharge is 1.0 ampere (17.2 ma/cm^2) for two hours. Low charge rate is 0.095 ampere (1.63 ma/cm^2) for twenty-two hours or 0.09 ampere (1.55 ma/cm^2) for twenty-four hours. Low rate discharge is the same as the low rate charge.

5. Voltage limits of 1.35 volts (cadmium vs. oxygen) as the upper limit will provide a reasonably complete charge for the three-electrode system. For the two-electrode system, the limit should be 1.65 volts (anode to cathode). This will have to be increased periodically because of the inherent properties of the cathode. A low limit setting of 0.4 volt (cadmium vs. oxygen) will give essentially complete discharge of either type cell.

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APPENDIX II

DESIGN STUDY

DESIGN STUDY FOR 28 VOLT - 3 KWH CADMIUM-OXYGEN RECHARGEABLE BATTERY NASA CONTRACT NAS-5-10384

SUMMARY

A design study, based on the cadmium-oxygen system, to determine the optimum weight and volume of a 28 volt - 3 KWH secondary metal-oxygen battery for spacecraft has been completed. The design is based on current knowledge derived from feasibility studies conducted under NASA Contract NAS-5-10384.

Calculations have been made for three charge/discharge regimes. The preliminary engineering layouts indicate the batteries may be contained in spherical tanks with auxiliary mechanisms mounted on three support legs. The estimated weight, size and power density figures are given in the following Table I.

TABLE I.

ESTIMATED WEIGHT, SIZE AND POWER DENSITY OF 28 VOLT - 3 KWH BATTERY

		CHARGE/DISCHARGE RATE		
		2 Hour	12 Hour	24 Hour
Battery Weight		130.62 lb.	104.36 lb.	100.28 lb.
Total Weight		191.68 lb.	158.93 lb.	153.53 lb.
Watt-Hr/lb	Battery	22.97	28.75	29.92
	Total	15.65	18.97	19.55
Internal Tank Diameter		20.92 in.	19.36 in.	19.12 in.
Total Volume		5105 in^3	4126 in^3	3928 in^3
Watt-Hr/in^3 (excluding external hardware)		0.59	0.73	0.76
Current Density		34.0 ma/cm^2	7.0 ma/cm^2	3.4 ma/cm^2

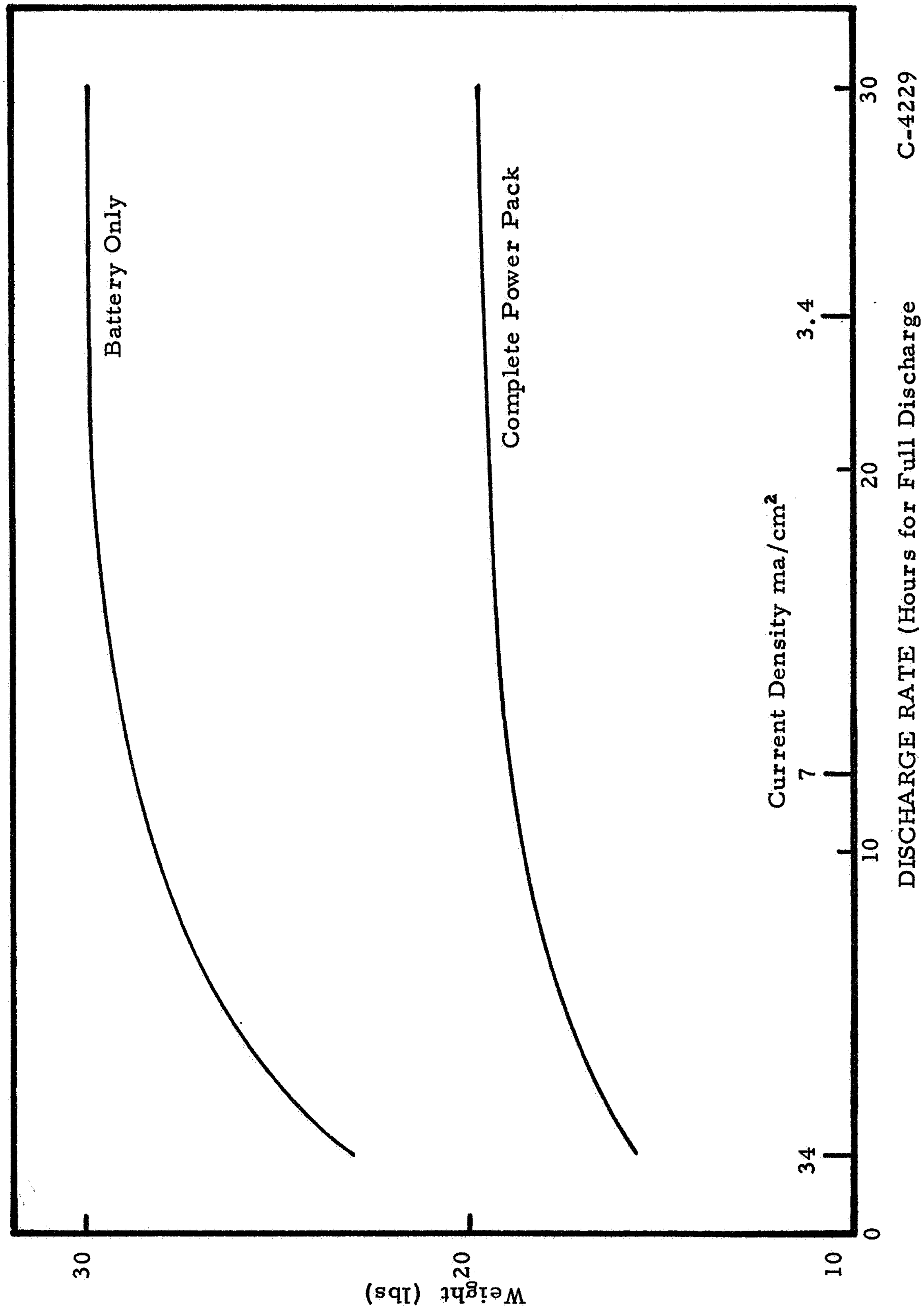
A plot of energy density versus discharge rate is given in Figure 1.

INTRODUCTION

In the development of power sources for spacecraft applications, considerable effort has been contributed to increasing the energy density of electrochemical systems in regard to on-board applications. While the theoretical

FIGURE 1.

ENERGY DENSITY VERSUS DISCHARGE RATE



maximum output for the active materials, in the case of the cadmium-oxygen system, reaches 268 watt-hours/pound, the reduction of the system to a practical operating rechargeable cell reduces this energy density value. This energy density is further reduced when the cells are packaged into a battery system complete with sustaining hardware.

NASA Contract NAS-5-10384 specifies a design study based on the cadmium-oxygen system to determine the optimum weight and volume of a sealed 28 volt - 3 KWH secondary battery discharged at a 24-hour rate followed by a 24-hour charge. In order to give a better picture of the capabilities of the system, the design study was expanded to include a two-hour and 12-hour rate study. The results of the feasibility study conducted under this contract form the basis for the design study.

Essentially, the power source is a cadmium-oxygen electrochemical system consisting of cells having a cadmium electrode, an alkaline electrolyte and a hydrophobic catalyzed oxygen electrode. The reactant, oxygen, is consumed during discharge and, when the system is recharged, the oxygen produced is returned to the reactant storage container.

The simplified electrode reactions which occur are,

Cadmium Anode $Cd + 2(OH)^- \rightarrow Cd(OH)_2 + 2e^-$

Oxygen Cathode $O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$

$H_2O + HO_2^- + 2e^- \rightarrow 3\,OH^-$

the net cell reaction is:

$$Cd + H_2O + \tfrac{1}{2} O_2 \overset{2e}{\rightleftarrows} Cd(OH)_2$$

WEIGHTS AND ENERGY DENSITY CALCULATIONS

A. Operating Parameters

The results of the feasibility studies, performed on the cadmium-oxygen rechargeable system and the power requirements of the contract, have indicated the following parameters used in the design study:

1. A 3 KWH, 28 volt battery will operate at 125 watts and 4.46 amperes for twenty-four hours, 250 watts and 8.93 amperes for twelve hours, and 1500 watts and 53.6 amperes for two hours.

2. The cadmium electrode operates at about 65% to 70% coulombic efficiency in thicknesses up to 0.085 inch. A lack of experimental work in excess of this thickness suggests a conservatively estimated limit of 0.100 inch for anode thickness.

3. The cadmium electrode in the discharged state is approximately 30% porous.

4. A cadmium anode 0.100 inch thick can provide a current of 52 ma/cm^2 for two hours, 8.6 ma/cm^2 for twelve hours and 4.3 ma/cm^2 for twenty-four hours.

5. The American Cyanamid LAB-40 electrode with B-II-4 backing can be used as the oxygen electrode on both charge and discharge. From polarization data, the upper limit of current density should be about 40 ma/cm^2 or less.

B. Weights and Density Summary

Based on the operating parameters, the design study has indicated the weights and power densities shown in Table II.

CELL DESIGN

A. Battery and Cell Requirements

For the specified 3 KWH battery requirement, the battery drains are governed by the discharge rate or cycle. Table III is a tabulation of the watt-hour and current drains for a 2-hr. charge/24-hr. discharge cycle. As indicated, for the maximum energy discharge rate of 1500 watts per hour, a 28-volt battery would have a current drain of 53.6 amperes.

Table IV is a tabulation showing the number of cells per battery and ampere-hours per cell based on the current density and the respective cell voltage.

B. Cell Construction

The cell design is based on the current knowledge derived from the feasibility study conducted on the cadmium-oxygen rechargeable system under the present contract and Union Carbide's background experience in fuel cell, AIR CELL and rechargeable battery systems. The cell design

TABLE II.

WEIGHTS AND ENERGY DENSITY SUMMARY - 28 VOLT - 3 KWH
CADMIUM-OXYGEN RECHARGEABLE BATTERY

Cell Component	Discharge Rate 2 Hours lb.		12 Hours lb.		24 Hours lb.		Text Reference
1. Battery (No. of Cells)	(38)		(33)		(32)		
a. Partition Plates	2.20		1.55		1.55		Table VIII
b. Cathodes	34.24		24.26		23.68		"
c. Cell Spacer (TEFLON)	4.41		3.10		3.04		"
d. Separator (PELLON)	0.84		0.59		0.58		"
e. Anode	61.37		53.56		50.69		"
f. Current Collectors	1.33		1.06		1.02		"
g. Electrolyte	23.29		17.69		17.25		"
h. Oxygen (+ 10%)	2.94		2.55		2.47		Sec. C, p. 13
Total Battery	130.62	130.62	104.36	104.36	100.28	100.28	
2. Battery Case	20.44		17.51		16.95		Sec. B, 7, p. 13
	20.44	151.06	17.51	121.87	16.95	117.23	
3. Tankage (Including Legs)	31.12		27.56		26.80		Sec. D, 5, p. 21
	31.12	182.18	27.56	149.43	26.80	144.03	
4. Hardware							
a. Pump	1.00		1.00		1.00		Sec. C, p. 16
b. Gas Liquid Separator	3.50		3.50		3.50		Sec. B, p. 16
c. Hydrogen Getter	1.00		1.00		1.00		Est.
d. Misc. Pipe and Fittings	4.00		4.00		4.00		Est.
	9.50	191.68	9.50	158.93	9.50	153.53	
Watt-Hours/Pound Battery		22.97		28.75		29.92	
Watt-Hours/Pound Total Weight		15.65		18.88		19.54	

TABLE III.

BATTERY CURRENT DRAINS FOR VARIOUS CYCLES

Discharge			Charge		
Hours	Watt/Hr.	Amp.	Hours	Watt/Hr.	Amp.
2	1500	53.6	2	1500	53.6
12	250	8.94	12	250	8.94
24	125	4.47	24	125	4.47

TABLE IV.

CELL REQUIREMENTS FOR 3 KWH - 28 VOLT BATTERY

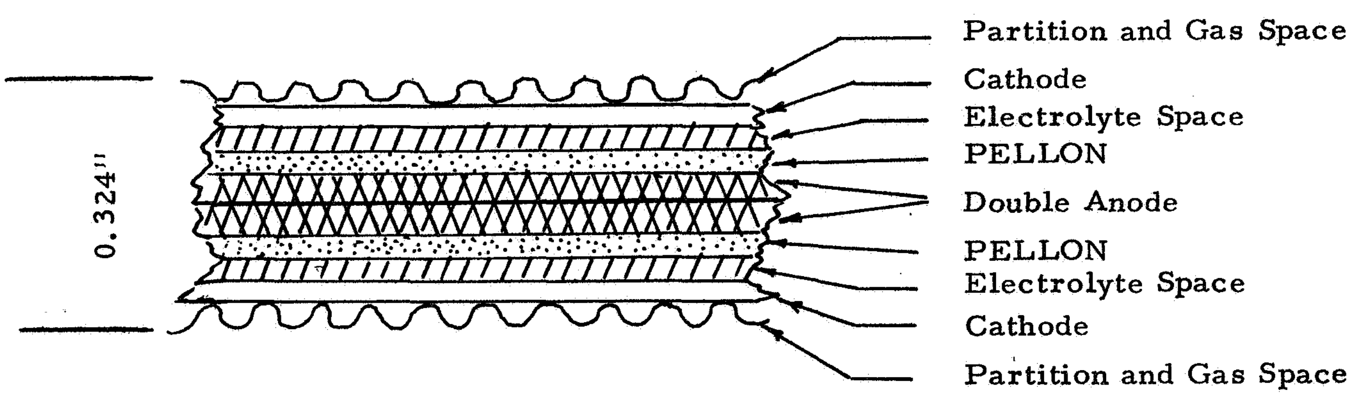
ma/cm^2	Cell Voltage	No. Cells for 28-volt Batt. Cal.	No.	Watt-Hrs.	Watt-Hrs. Per Cell	Amp-Hr. Per Cell	Amp-Hr. Per Batt.
1.7	0.90	31.1	32	3000	96.5	107.1	3427.2
3.4	0.88	31.8	32	3000	94.3	107.1	3427.2
7.0	0.85	33.0	33	3000	91.0	107.1	3534.3
17.0	0.80	35.0	35	3000	85.7	107.1	3748.5
34.0	0.74	37.8	38	3000	79.3	107.1	4069.8

concept shown in Figure 2 is based on the utilization of the American Cyanamid LAB-40 oxygen electrode as the positive electrode, and an electrodeposited cadmium negative electrode. A PELLON separator is used to enclose the anode and separate the working electrodes.

The electrolyte space is maintained by expanded TEFLON spacers between the cathode and the PELLON separator. A space is provided between the cathodes of each cell and the partition, which serves as a channel to allow oxygen access to the cathodes. Metal collector tabs are attached to the electrodes. These tabs enable external electrical connections to be made such as parallel connection of the dual cathodes and anodes in each cell as well as series connection of the cells in the battery.

FIGURE 2.

CADMIUM-OXYGEN DUAL CATHODE AND ANODE CELL CROSS SECTION



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C. Cathode

1. Description

Two types of cathode material have been evaluated. The Union Carbide "fixed zone" material consisting of an active carbon layer applied to one side of a porous metal backing and the American Cyanamid LAB-40 electrode material.

The Union Carbide T-2 electrode is used only as the oxygen electrode and is not used in the charging circuit because oxygen evolved on its catalyzed carbon surface oxidizes the carbon to form soluble quinone type compounds. This would destroy the hydrophobic nature of the electrode and make it susceptible to flooding. With the T-2 electrode, a separate nickel charging electrode is used so that the oxygen will be evolved at this electrode and will not have an opportunity to react with the active face of the oxygen electrode. While satisfactory results have been obtained with this system of electrodes, its use in a workable battery would involve added weight and volume because of additional battery components as well as additional hardware which would be necessary to switch electrodes during the charge or discharge portion of the cycle.

The LAB-40 electrode can be used as the active electrode on both charge and discharge. Therefore, in order to eliminate the third electrode and complimentary hardware, the design study has incorporated the American Cyanamid LAB-40 oxygen electrode as an integral part of the system.

2. Cathode Area and Size

Feasibility studies have indicated reliable cathode service at current densities up to 34 ma/cm^2. The operating voltage decreases with increasing current density. In order to use a thicker anode, as discussed later, it is deemed advisable to use a dual cathode cell, in other words, to use a cathode on each side of a relatively thick anode. The electrode dimensions and area required to carry various loads are given in Table V.

D. Separators

A nonwoven nylon material is used to physically separate the electrodes. PELLON 10194C and 2505W have been shown to be satisfactory for this function. PELLON 2505W is better suited for control of dendrite growth and is the preferred material for the proposed battery.

TABLE V.

CATHODE SIZE AND AREA FOR DUAL CATHODE CELLS

Current Density ma/cm²	2 Hr. Discharge			12 Hr. Discharge			24 Hr. Discharge		
	Size	Area		Size	Area		Size	Area	
	Inches Per Edge	One Electrode (in^2)	Two Electrodes (in^2)	Inches Per Edge	One Electrode (in^2)	Two Electrodes (in^2)	Inches Per Edge	One Electrode (in^2)	Two Electrodes (in^2)
1.7	49.40	2440	4880	20.19	408.0	816.0	14.28	204.0	408.0
3.4	34.92	1220	2440	14.28	204.0	408.0	10.10	102.0	204.0
7.0	24.35	595	1190	9.97	99.3	199.0	7.04	49.5	99.0
17.0	15.62	244	488	6.12	40.8	81.6	4.52	20.4	40.8
34.0	11.06	122	244	4.52	20.4	40.8	3.34	10.2	20.4
Total Current		53.57 amperes			8.94 amperes			4.47 amperes	
Current per Electrode		26.78 amperes			4.47 amperes			2.235 amperes	

E. Spacers

In order to maintain pressure on the anode, a TEFLON web material is used. Positioned between the oxygen and cadmium electrodes, it also serves to define the thickness of the electrolyte space.

A corrugated plastic member is used to define the gas space behind the cathode and also serves as a partition between cells. The material must be nonporous, electrolyte resistant and relatively rigid. Polypropylene or polysulfone would be suitable for this application.

F. Anode

The anode proposed for the battery is the Union Carbide electrodeposited cadmium electrode, in which cadmium is deposited on a nickel screen or mesh. Other base materials such as copper, silver or iron may be used if desired. This anode operates at about 65 to 70 per cent coulombic efficiency. Thus an anode with physical dimensions of 3'' x 3'' x 0.030'', electrodeposited by the passage of 3.08 ampere-hours of current will on discharge deliver approximately 2.0 to 2.2 ampere-hours and would weigh 13.5 grams in the discharge state. Conservatively, we will use the 2.0 ampere-hours value and derive anode volume and weight factors as follows:

$$\frac{3'' \times 3'' \times 0.030''}{2.0} = 0.135 \text{ in}^3 \text{ of anode per amp-hr}$$

$$\frac{13.5}{2.0} = 6.75 \text{ grams of anode per amp-hr}$$

With these factors we calculate anode parameters as shown in Table VI.

The coulombic efficiency of the cadmium electrode is reduced with excessively thick anodes and therefore the anode thickness should not exceed about 0.10 inch. By using a cathode on each side, the total anode thickness could be increased to 0.20 inch as a maximum design value.

Since all components of a cell are of a fixed thickness except for the anode, it is possible to determine cell geometry by proper choice of discharge current density. This fixes the necessary anode area and thickness to give the required ampere-hour capacity. A summation of the effect of anode thickness on total battery shape is given in Table VII for the various current densities used previously in this discussion.

TABLE VI.

CALCULATED ANODE WEIGHT, VOLUME AND THICKNESS AT VARIOUS CURRENT DENSITIES

Current Density ma/cm²	Actual Amp-Hr per Cell	Anode Volume in³ per Cell (A-Hr x 0.135)	Anode Weight lbs/Cell (A-Hr x 6.75)	Anode Thickness for Various Rates Vol. ÷ Area (from Table V)		
				2-Hr Discharge	12-Hr Discharge	24-Hr Discharge
1.7	107.1	14.43	1.592	0.0059 in.	0.0354 in.	0.0708 in.
3.4	107.1	14.43	1.592	0.0118 "	0.0708 "	0.1416 "
7.0	107.1	14.43	1.592	0.0243 "	0.1453 "	0.2906 "
17.0	107.1	14.43	1.592	0.0509 "	0.3537 "	0.7074 "
34.0	107.1	14.43	1.592	0.1182 "	0.7074 "	1.4148 "

TABLE VII.

EFFECT OF CURRENT DENSITY ON ANODE SIZE AND BATTERY GEOMETRY

Current Density ma/cm²	Av. Volts Table IV.	No. of Cells	Battery Length Less Anode	2-Hour Discharge			12-Hour Discharge			24-Hour Discharge		
				Anode Thickness Table VI	Batt. Length	Length-to-Side Ratio*	Anode Thick. Table VI	Batt. Length	Length-to-Side Ratio*	Anode Thick. Table VI	Batt. Length	Length-to-Side Ratio*
1.7	0.90	32	5.57 in.	0.0059 in.	5.79 in.	0.117	0.0354 in.	6.74 in.	0.334	0.0708 in.	7.83 in.	0.548
3.4	0.88	32	5.57 "	0.0118 "	6.02 "	0.172	0.0708 "	7.91 "	0.553	0.1416 "	10.10 "	1.000
7.0	0.85	33	5.74 "	0.0243 "	6.66 "	0.273	0.1453 "	10.53 "	1.057	0.2906 "	15.04 "	2.140
17.0	0.80	35	6.09 "	0.0509 "	8.02 "	0.513	0.3537 "	17.76 "	2.900	0.7074 "	28.73 "	6.350
34.0	0.74	38	6.61 "	0.1182 "	11.10 "	1.002	0.7074 "	29.95 "	6.625	1.4148 "	51.88 "	15.530

* Battery length divided by length of electrode side from Table V.

To give better packaging capability, we have chosen to use a battery pack which is as nearly cubic as possible. Therefore, a battery length-to-side ratio of 1:1 is desired and the operating current density for the battery can be chosen from Table VI.

BATTERY DESIGN

A. Description

The proposed battery construction would consist of cells individually assembled as units and stacked to form the battery. At the time of the stack assembly, the individual terminal tabs are connected. The entire battery is potted in epoxy resin with suitable porting for oxygen circulation.

Gas evolution at the proposed current densities has been very low on the electrolyte side of the American Cyanamid electrode. The electrode structure is such that most of the oxygen is evolved from the back surface. There is, however, some gas evolution into the electrolyte. Some of this gas is oxygen and some is hydrogen from the anode. In a sealed system as is proposed here, circulation of electrolyte through all cell cavities of the battery will remove gas and compensate for changes in electrolyte volume caused by gas generation. The flow of electrolyte through each cell requires channels in the battery package to evenly distribute and collect the circulating liquid. A hydrogen getter will be provided in the system to keep hydrogen concentrations well below hazardous levels.

B. Battery Package Calculations

1. Cross Sectional Dimensions	2-Hr Rate	12-Hr Rate	24-Hr Rate
Maximum Cell Component Dimension	11.31 in.	10.22 in.	10.25 in.
0.500 in. Case Wall x 2	1.00	1.00	1.00
Battery Case Width & Height	12.31 in.	11.22 in.	11.25 in.

2. End Plates

Material: PANELYTE No. 161
Epoxy Impregnated Glass Cloth

Density: 0.068 lb/in^3

2 pieces Length x Width x 0.025 in.	75.77 in^3	62.94 in^3	63.35 in^3
Volume x 0.068 lb/in^3	5.15 lb	4.28 lb	4.30 lb

	2-Hr Rate	12-Hr Rate	24-Hr Rate
3. Battery Package Length			
Unit Cell Thickness (Table VIII x No. of cells [Table VII]) =	11.11 in.	10.56 in.	10.10 in.
Plus 2 end plates 0.025 in. each	0.50	0.50	0.50
Battery Package Length	11.61 in.	11.06 in.	10.60 in.
4. Battery Package Volume			
Length x Width x Height	1759.37 in^3	1392.34 in^3	1341.56 in^3
5. Battery Component Volume and Weight			
Unit Cell volume (Table VIII) x No. of cells	1381.30 in^3	1067.88 in^3	1028.16 in^3
Unit Cell weight (Table VIII) x No. of cells	127.68 lb.	101.80 lb	97.76 lb
6. Epoxy Potting Resin			
Material Density: 0.0506 lb/in^3			
(Battery Package Volume) -(Battery Component Volume + End Plate Volume) = Resin Volume:	302.30 in^3	261.52 in^3	250.05 in^3
Resin Volume x 0.056 = Resin Wt.	15.29 lb	13.23 lb	12.65 lb
7. Battery Case Material			
Resin Volume + End Plate Volume =	378.07 in^3	324.46 in^3	313.40 in^3
Resin Weight + End Plate Weight =	20.44 lb	17.51 lb	16.95 lb

C. Oxygen Requirements

Table IX is a tabulation of the calculated cell requirements for a 3 KWH operation and with 10 per cent excess oxygen.

Oxygen requirements based on:

0.298 g O_2/amp-hr (theoretical)

$$\frac{0.298\ g \times 22.4\ (l/mole)}{32\ g/mole} = 0.2088 \text{ liters (STP)/amp-hr}$$

TABLE VIII.

CELL COMPONENTS - WEIGHTS & VOLUMES

Cell Component	No. /Cell	Dimensions (in.) Long	x Wide	x Thick	Density Lb. /in^3.	Area One Side (in^2)	Volume Total (in^3)	Weight Total (lb)
2-Hour Discharge - 34 ma/cm^2								
Partition	1	11.31	11.31	0.010	0.0450	127.92	1.28	0.058
Cathode	2	11.31	11.31	0.032	0.1101	127.92	8.18	0.901
(Gas Space)	2	11.06	11.06	0.010	------	------	2.45	-----
Cell Spacer (TEFLON)	2	11.06	11.06	0.030	0.0158	122.32	7.34	0.116
(Electrolyte)	2	-----	-----	-----	0.0506	------	(5.50)	0.278
Separator (PELLON)	2	11.31	11.31	0.100	0.0087	127.92	2.56	0.022
(Electrolyte)	2	-----	-----	-----	0.0506	------	(2.30)	0.116
Anode	2	11.06	11.06	0.059	0.1119	122.32	14.43	1.615
(Electrolyte)	2	-----	-----	-----	0.0506	------	(4.33)	0.219
Current Collectors (Ni)	4	11.31	0.25	(0.010)	0.3193	2.83	0.11	0.035
Total Length, Volume & Weight/Cell				0.292 in.			36.35 in^3	3.360 lb.
12-Hour Discharge - 7.0 ma/cm^2								
Partition	1	10.22	10.22	0.010	0.0450	104.45	1.04	0.047
Cathode	2	10.22	10.22	0.032	0.1101	104.45	6.68	0.735
(Gas Space)	2	9.97	9.97	0.010	------	------	1.99	-----
Cell Spacer (TEFLON)	2	9.97	9.97	0.030	0.0158	99.40	5.96	0.094
(Electrolyte)	2	-----	-----	-----	0.0506	------	(4.47)	0.226
Separator (PELLON)	2	10.22	10.22	0.010	0.0087	104.45	2.09	0.018
(Electrolyte)	2	-----	-----	-----	0.0506	------	(1.90)	0.096
Anode	2	9.97	9.97	0.073	0.1119	99.40	14.50	1.623
(Electrolyte)	2	-----	-----	-----	0.0506	------	(4.24)	0.214
Current Collectors (Ni)	4	10.22	0.25	(0.010)	0.3193	2.56	0.10	0.032
Total Length, Volume & Weight/Cell				0.320 in.			32.36 in^3	3.085 lb.
24-Hour Discharge - 3.4 ma/cm^2								
Partition	1	10.25	10.25	0.010	0.0450	105.06	1.05	0.047
Cathode	2	10.25	10.25	0.032	0.1101	105.06	6.72	0.740
(Gas Space)	2	10.00	10.00	0.010	------	------	2.00	-----
Cell Spacer (TEFLON)	2	10.00	10.00	0.030	0.0158	100.00	6.00	0.095
(Electrolyte)	2	-----	-----	-----	0.0506	------	(4.50)	0.228
Separator (PELLON)	2	10.25	10.25	0.010	0.0087	105.06	2.10	0.018
(Electrolyte)	2	-----	-----	-----	0.0506	------	(1.90)	0.096
Anode	2	10.00	10.00	0.071	0.1119	100.00	14.16	1.584
(Electrolyte)	2	-----	-----	-----	0.0506	------	(4.25)	0.215
Current Collectors (Ni)	4	10.25	0.25	(0.010)	0.3193	2.56	0.10	0.032
Total Length, Volume & Weight/Cell				0.316 in.			32.13 in^3	3.055 lb.

TABLE IX.

OXYGEN REQUIREMENTS FOR 3 KWH-28 VOLT BATTERY

ma/cm^2	Amp-Hr Per Cell	No. of Cells	Amp-Hr Per Batt.	Oxygen Wt-g	Oxygen Vol-liter	Oxygen + 10% Wt-g	Oxygen + 10% Wt-lb	Oxygen + 10% Vol-liter
1.7	107.1	32	3427.2	1022.0	717	1124.2	2.47	788.7
3.4	107.1	32	3427.2	1022.0	717	1124.2	2.47	788.7
7.0	107.1	33	3534.3	1053.0	739	1158.3	2.55	812.9
17.0	107.1	35	3748.5	1117.0	783	1228.7	2.70	861.3
34.0	107.1	38	4069.8	1215.0	851	1336.5	2.94	936.0

SYSTEM DESIGN

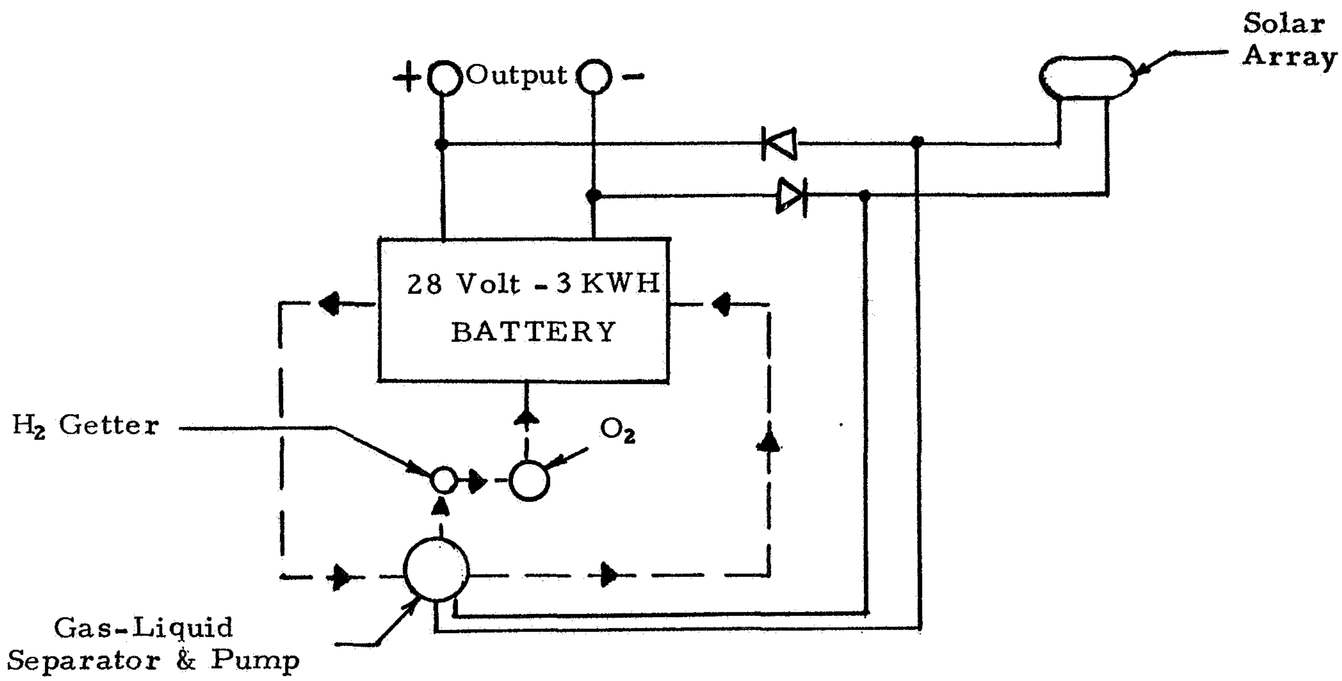
A. Description

The schematic diagram, Figure 3, shows the proposed power system as it would operate from the solar array. By circulating the electrolyte through each cell of the battery, it will be possible to remove any gas generated during the charging cycle. A centrifuge is provided for gas-liquid separation. After the point of gas separation, a getter will be used to remove hydrogen from the oxygen gas prior to its return to the reactant tankage.

It is also proposed to enclose the battery package within the reactant (oxygen) storage tank to further conserve on space and weight. The electrolyte pump would necessarily be mounted outboard of the tank to lessen the danger of combustion due to operation of the electrical pump motor in the oxygen atmosphere.

FIGURE 3.

SCHEMATIC DIAGRAM OF THE PROPOSED POWER SYSTEM



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B. Gas-Liquid Separator

Under Contract NAS-3-4930, Union Carbide subcontracted Air Research Manufacturing Company, a division of the Garrett Corporation, for an experimental feasibility study of bubble separators. Their work showed very positive results with a cyclone-type separator and the proposed design here is based on a similar device.

C. Electrolyte Pump

The Fuel Cell Department of the Electronics Division of the Union Carbide Corporation has developed small electrolyte pumps which could be applied to this system. The nature of the electric motor-operated pump dictates its use outboard of the reactant tankage. It is assumed that spacecraft in which this power system would be employed would have an electric inverter onboard and that a small quantity of power could be diverted to operate the

AC pump motor.

D. Tankage

The system containment vessel is designed with a safety factor of 3.3 based on yield strength. The construction material will be 6061-T aluminum alloy having a working stress of 33,000 psi and a material density of 0.1 lb/in^3, all interior tank surfaces to be coated with nickel or a suitable plastic to prevent chemical attack by the environment. Using these values, thickness requirements for the vessels have been calculated for the pressures expected. Each flange to be one-half inch thick by one inch in width welded to each spherical half section. The support legs are one quarter inch thick having cutouts for hardware mounting and weight reduction. The tankage weight summary is shown in Table X.

TABLE X.

SUMMARY OF TANK VOLUMES & WEIGHTS

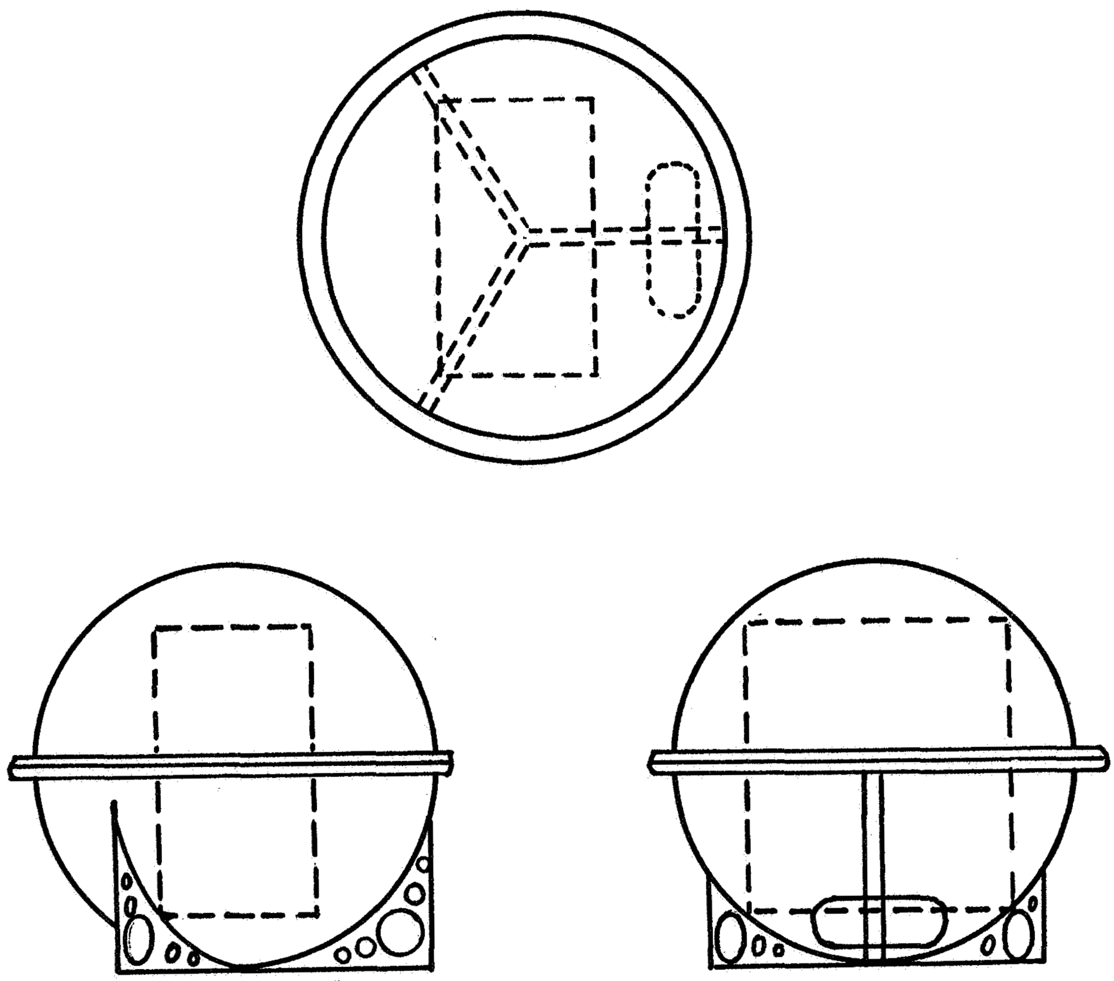
	Design for Discharge Rate of		
	2-Hr Rate	12-Hr Rate	24-Hr Rate
Total Volume Spherical Tank	5027.26 in^3	4126.16 in^3	3858.06 in^3
Volume Tank Shell	233.20 "	203.71 "	198.05 "
Volume Flanges (2)	69.92 "	65.50 "	64.33 "
Volume Legs (3)	8.10	6.35 "	5.63 "
Total Volume Tank Metal	311.22 in^3	275.56 in^3	268.01 in^3
Total Volume Tankage	5105.28 in^3	4198.01 in^3	3928.02 in^3
Weight of Tankage	31.12 lb	27.56 lb	26.80 lb

1. Tankage Structure

A preliminary design of the reactant tankage, containing the battery system, has been developed as shown in the three views of Figure 4. The containment vessel is a half-sectioned sphere, the bottom section having three support legs into which are mounted the electrolyte pump and gas-liquid separator. The battery is mounted in the spherical sections and kept in position by small corner mounts. The two flanged half-sections are bolted together to effect pressurization.

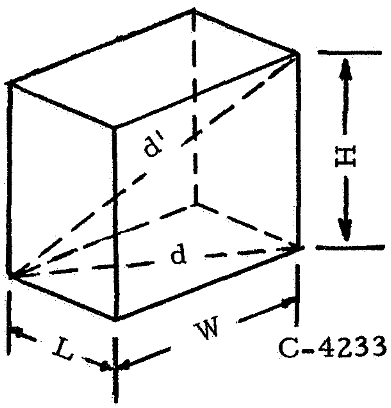
FIGURE 4.

TANKAGE STRUCTURE



2. Tank Diameter

Figure 5. - Battery Dimensions



	2-Hour Rate	12-Hour Rate	24-Hour Rate
H	12.31 in.	11.22 in.	11.25 in.
W	12.31 in.	11.22 in.	11.25 in.
L	11.61 in.	11.06 in.	10.60 in.

For all four corners of the battery to touch the inner surface of the spherical container, the diameter of the sphere must equal the diameter (d') of the battery.

H = Heighth
W = Width
L = Length

$$d = \sqrt{W^2 + L^2}$$

$$d' = \sqrt{d^2 + H^2}$$

$$d' = \sqrt{W^2 + L^2 + H^2} = \quad 20.92 \text{ in.} \quad 19.36 \text{ in.} \quad 19.12 \text{ in.}$$

3. Internal Tank Volume

Volume of spherical tank (r = 1/2 I. D.)

$$4.189\ r^3 = \quad 4794.06 \text{ in}^3 \quad 3799.59 \text{ in}^3 \quad 3660.01 \text{ in}^3$$

4. Oxygen Storage Volume & Calculated Pressure

	2-Hour Rate	12-Hour Rate	24-Hour Rate
Internal volume of sphere (D-3) less Battery package volume (B-4, p. 13)	3034.69 in^3	2407.25 in^3	2318.45 in^3
Cubic inches x 0.01639 = Liters	49.74 L	39.45 L	38.00 L
$P' = \frac{PVT'}{V'T} =$	317.50 psi	347.00 psi	349.80 psi

where:

V = Vol. O_2 required standard temperature and pressure.

V' = O_2 storage volume in tank.

P = Standard atmospheric pressure (14.7 psi).

P' = O_2 pressure in tank at 40° C.

T = Standard temperature (273° K)
T' = 313° K (40° C)

5. Tankage Weight Calculations

a. Material

Aluminum Alloy - 6061-T

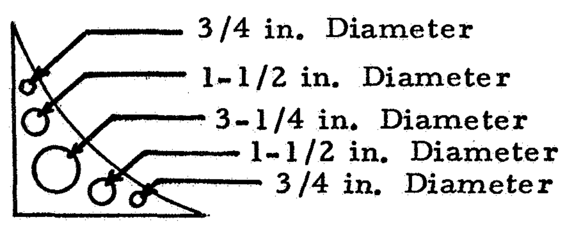
Working Stress - 33,000 psi

Density - 0.10 lb/in^3

b. Required Wall Thickness	2-Hr. Rate	12-Hr. Rate	24-Hr. Rate
Working pressure (D-4, p. 20) x Safety Factor of 3.3 = P =	1056.0 psi	1155.0 psi	1155.0 psi
I. D. of Sphere (D-2, p. 20) = d =	20.92 in.	19.36 in.	19.12 in.
Wall Thickness = w = $\frac{Pd}{4 \times 33{,}000}$	0.167 in.	0.169 in.	0.167 in.
c. Volume of Metal in Sphere Wall			
Vol. Wall = 4.189 $[(r + w)^3 - r^3]$	233.20 in^3	203.71 in^3	198.05 in^3
d. Volume of Flanges			
2 pieces 1/2 in. thick x 1.0 in. wide			
2 x 0.5 x 0.7854 $[(d + 2w + 2.0) - (d + 2w)]$ =	69.92 in^3	65.50 in^3	64.33 in^3

e. Volume of Legs

Figure 6. Support Leg Pattern



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General equation for area of a leg without cutouts is:

$$a = \frac{d^2 - 0.7854\ d^2}{4} =$$

	2-Hr. Rate	12-Hr. Rate	24-Hr. Rate
a	23.48 in^2	21.14 in^2	20.19 in^2
Area of cutouts	12.68 in^2	12.68 in^2	12.68 in^2
Area of Finished Leg A	10.80 in^2	8.46 in^2	7.51 in^2
Volume of Legs = A x 0.25 in. x 3 =	8.10 in^3	6.35 in^3	5.63 in^3

f. Total Weight of Tankage	2-Hour Rate	12-Hour Rate	24-Hr. Rate
Total Tankage Volume = Sphere Wall + Flanges + Legs =	311.22 in^3	275.56 in^3	268.01 in^3
Volume x 0.10 lb/in^3 =	31.12 lb	27.56 lb	26.80 lb

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Attn: Dr. Eugene Willihnganz
Division of Electic Autolite Co.
Conshohocken, Pennsylvania 19428

Calvin College, Science Bldg.
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3175 Burton St., S.E.
Grand Rapid, Michigan 49506

Catalyst Research Corporation
Attn: H. Goldsmith
6101 Falls Road
Baltimore, Maryland 21209

Communications Satellite Corporation
Attn: Mr. Robt. Strauss
1835 K Street N.W.
Washington, D.C. 20036

G. & W. H. Corson, Inc.
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Plymouth Meeting
Pennsylvania 19462

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Delco Remy Division
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General Motors Corporation
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Anderson, Indiana 46011

E. I. du Pont Nemours & Co.
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Engineering Materials Laboratory
Experimental Station, Building 304
Wilmington, Delaware 19898

ESB Inc.
Attn: Director of Engineering
P.O. Box 11097
Raleigh, North Carolina 27604

ESB Inc.
Attn: Dr. R. A. Schaefer
Carl F. Norberg Research Center
19 West College Avenue
Yardley, Pennsylvania 19067

Eagle-Picher Company
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Post Office Box 47
Joplin, Missouri 64801

Electrochimica Corporation
Attn: Dr. Morris Eisenberg
1140 O'Brien Drive
Menlo Park, California 94025

Electromite Corporation
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2117 South Anne Street
Santa Ana, Calif. 92704

Electro-Optical Systems, Inc.
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300 North Halstead Street
Pasadena, California 91107

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Box 1620
Hartford, Connecticut 06102

Dr. Arthur Fleischer
466 South Center Street
Orange, New Jersey 07050

General Electric Company
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Research and Development Center
P.O. Box 43
Schenectady, New York 12301

General Electric Company
Attn: K. L. Hanson, Rm M-2614
Missile & Space Division
Spacecraft Dept.
P.O. Box 8555
Philadelphia, Pennsylvania 19101

General Electric Company
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Battery Business Section
P.O. Box 114
Gainsville, Florida 32601

General Electric Company
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Schenectady, New York 12301

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P.O. Box 591
Milwaukee, Wisconsin 53201

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Plant 25
AAP Project-Future Missions
Bethpage, L.I.N.Y. 11714

Gulton Industries
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Alkaline Battery Division
1 Gulton St.
Metuchen, New Jersey 08840

Honeywell Inc.
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Livingston Electronic Laboratory
Montgomeryville, Pa. 18936

Dr. P. L. Howard
Centreville, Maryland 21617

Hughes Aircraft Corporation
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Bldg. 366, M.S. 524
El Segundo, California 90245

IIT Research Institute
Attn: Dr. H. T. Francis
10 West 35th Street
Chicago, Illinois 60616

Idaho State University
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Pocatello, Idaho 83201

Institute for Defense Analyses
Attn: Mr. R. Hamilton
400 Army-Navy Drive
Arlington, Virginia 22202

Institute for Defense Analyses
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International Nickel Co.
Attn: Wm. C. Mearns
1000-16th St., N.W.
Washington, D.C. 20036

Johns Hopkins University
Attn: Richard E. Evans
Applied Physics Laboratory
8621 Georgia Avenue
Silver Spring, Maryland 20910

Leesona Moos Laboratories
Attn: Dr. A. Moos
Lake Success Park, Community Drive
Great Neck, New York 11021

Arthur D. Little, Inc.
Attn: Dr. James D. Birkett
Acorn Park
Cambridge, Massachusetts 02140

Lockheed Missile and Space Company
Attn: Robert E. Corbett
Department 62-14, Bld. 154
P.O. Box 504
Sunnyvale, California 94088

Mallory Battery Company
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So. Broadway & Sunnyside Lane
Tarrytown, New York 10591

P. R. Mallory & Co., Inc.
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Northwest Industrial Park
Burlington, Massachusetts 01801

P. R. Mallory & Co., Inc.
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M. S. Imamura, MS 8840
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Denver, Colorado 80201

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Attn: John H. Waite
Montgomeryville Industrial Center
Montgomeryville, Pa. 18936

McDonnell Douglas
Attn: Dr. George Moe
Astropower Laboratory
2121 Campus Drive
Newport Beach, California 92663

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Texas Instruments Inc.
34 Forest Street
Attleboro, Massachusetts 02703

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New Enterprise Div.
Everett, Massachusetts 02149

North American Aviation Co.
Attn: Dr. James Nash
S&ID Division
Downey, California 90241

Philco-Ford Corporation
Attn: Mr. D. C. Briggs
Space Power & Prop. Dept. M.S. W-49
3825 Fabian Way
Palo Alto, California 94303

Power Information Center
University City Science Institute
3401 Market St., Rm. 2107
Philadelphia, Pennsylvania 19104

Prime Battery Corp.
15600 Cornet St.
Santa Fe Springs, Calif. 90670

RAI Research Corp.
36-40 37th Street
Long Island City, N.Y. 11101

Sonotone Corporation
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Southwest Research Institute
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San Antonio, Texas 78206

TRW Systems, Inc.
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One Space Park
Redondo Beach, California 90278

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One Space Park (R-1/2094)
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TRW, Inc.
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Tyco Laboratories, Inc.
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Bear Hill
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Union Carbide Corporation
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P.O. Box 6116
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Philadelphia, Pennsylvania 19104

Westinghouse Electric Corporation
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Research and Development Center
Churchill Borough
Pittsburgh, Pennsylvania 15235

Whittaker Corporation
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3850 Olive Street
Denver, Colorado 80237

Whittaker Corporation
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